LOAN COPY

PINEDALE TX

Precipitation and Lake Chemical Composition

in the Wind River Mountains of Wyoming:

Analysis of U.S. Forest Service and NADP Data Sets

A report submitted to the USDA Forest Service Bridger Teton National Forest

1 March 1996

Jill Baron, Ph.D.
National Biological Service
Natural Resource Ecology Laboratory
Colorado State University
Fort Collins, Colorado 80523
970-491-1968
jill@nrel.ColoState.edu

Precipitation and Lake Chemical Composition

in the Wind River Mountains of Wyoming:

Analysis of U.S. Forest Service and NADP Data Sets

Jill Baron, Ph.D.
National Biological Service
Natural Resource Ecology Laboratory
Colorado State University
Fort Collins, CO 80523,

1.0 INTRODUCTION

The Bridger-Teton National Forest began a program of lake sampling in the Wind River Mountains in 1984 to document water quality and monitor trends with time. Because the Wind Rivers are granitic, steep, and poorly vegetated, USDA Forest Service managers were concerned that surface waters in these mountains were susceptible to and possibly receiving acidic atmospheric deposition. Five low ANC wilderness lakes in the Bridger-Fitzpatrick and Popo-Agie Wilderness Areas were selected by the Forest Service as representative regional examples to evaluate potential impacts of acidic deposition. Saddlebag, Deep, and Black Joe Lakes are located south of Pinedale WY, while Hobbs and Ross Lake are located north of Pinedale (Figure 1).

The purpose of this report is to present an evaluation of the Forest Service data set collected between 1984 and 1993. Water quality was examined at the five study lakes in light of regional precipitation chemistry. Precipitation was analyzed from four
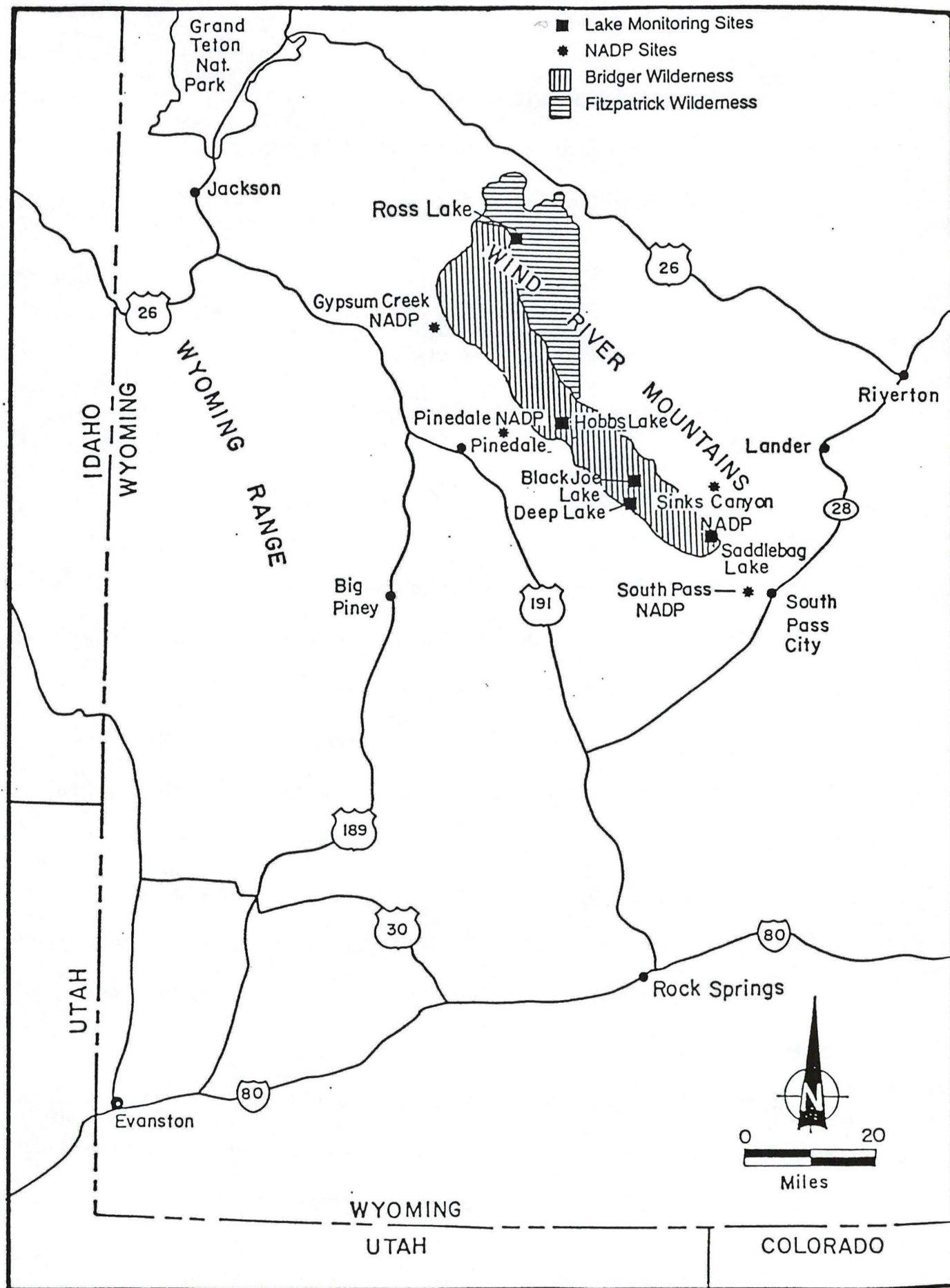
Fig. 1. Map of southwest Wyoming monitoring sites.

Precipitation and Lake Chemical Composition

in the Wind River Mountains of Wyoming:

Analysis of U.S. Forest Service and NADP Data Sets

A report submitted to the USDA Forest Service Bridger Teton National Forest

1 March 1996

Jill Baron, Ph.D.
National Biological Service
Natural Resource Ecology Laboratory
Colorado State University
Fort Collins, Colorado 80523
970-491-1968
jill@nrel.ColoState.edu

TABLE OF CONTENTS

National Atmospheric Deposition Program collection sites located around the Wind River Mountains at elevations ranging 2100-2500 m, and from bulk precipitation collectors located at Hobbs and Black Joe Lakes (Figure 1).

In a previous analysis of these data Welker (1994) found no significant difference in the chemical composition of water sampled from lake inlet, outlet, and at different lake depths, and recommended the number of sampling locations at each lake could be reduced. Welker further recommended that the number of lake sample dates per year could be reduced, based on the finding that the water was not significantly different from one sample date to the next during the ice-free season. Welker did not recommend reducing the number os lakes sampled each year, since there are only five lakes that are now used to represent the entire Wind River Mountain range. If the number of lakes had to be reduced, she suggested eliminating the largest lake, Ross Lake, and Hobbs Lake, which has a wetland upstream that sequesters nitrogen.

2.0 METHODS

2.1. Forest Service Field Techniques

2.1.a. Surface Water Samples

U.S. Forest Service technicians collected lake samples from Deep, Black Joe, and Hobbs Lakes beginning in 1984. Ross Lake sampling began in 1985, and Saddlebag Lake was added to the program in 1986. After 1986 lakes were sampled 2-4 times each year, between May and October. Water samples were taken from the

inlet and outlet streams, and from the epilimnion and hypolimnion layers of each lake. Approximately 10% of the yearly samples were collected in duplicate beginning in 1985.

From 1984-1990 water samples were collected in acid washed HDPE bottles. Samples were transported to the Forest Service District Office in Pinedale, WY, where aliquots were split for different chemical analyses. Untreated samples were used for laboratory analyses of alkalinity. Water for cation analyses was filtered (0.45 μm) and acidified; aliquots for anion analysis were filtered into dark, unacidified bottles. Samples collected from 1984-1990 were shipped to the USGS central analytical laboratory in Arvada, Colorado, where they were analyzed using methods of Fishman and Friedman (1985).

From 1991-1994 water samples were analyzed at the USFS Rocky Mountain Range and Experimental Station in Fort Collins, Colorado. Pre-washed dark 250 mL Nalgene bottles filled with deionized water were shipped from the Fort Collins laboratory. Bottles were emptied of DI water at the sample site, and rinsed three times with sample before filling. Conductivity and pH were analyzed in Pinedale using the same methods as for NADP precipitation samples (Bigelow and Dossett 1988). The remainder of the sample was split into filtered (0.45 μm) and unfiltered aliquots before shipping to the Fort Collins laboratory for analyses for major anions and cations. Laboratory methods used at the USFS laboratory are described in O'Deen et al. (1993). More details on field, laboratory, and quality assurance procedures are given in the AQRV Report #2 (Galbraith et al. 1991).

2.1.b. Weekly Wet Deposition

Precipitation samples were collected weekly through the National Atmospheric Deposition Program/National Trends Network (NADP/NTN 1994). This national precipitation monitoring program adheres to strict sampling and analytical protocols (Aubertin et al. 1990). Complete sample collection years (calendar years) are available from 1982 at Pinedale (site WY06, elevation 2388 m), 1985 at Gypsum Creek (WY98, elevation 2428 m), and Sinks Canyon (WY02, elevation 2164 m), and 1986 for South Pass City (WY97, elevation 2511 m) NADP/NTN sites. All the NADP/NTN precipitation chemistry samples were analyzed at the NADP's central analytical laboratory at the Illinois State Water Survey (Peden 1986).

2.1.c. Bulk Precipitation

Bulk precipitation was collected at Black Joe and Hobbs Lakes since 1986. Sampling frequency was twice a month during months of primarily rainfall, June through September. Sampling frequency during the remainder of the year was every two-three months from 1986-1991, and monthly after that.

During summer months rain collectors were 2 L bottles connected to a 10-inch funnel with tubing. Collector bottles were stored full of de-ionized water prior to use. Funnel and tubing were rinsed three times with de-ionized water at every collection period. Sample bottles that had been collecting rain were replaced with empty, rinsed bottles.

Snow collectors consisted of 18-inch galvanized steel tubes that supported large plastic bags. Collections were triple-bagged to minimize contamination and

breakage. Because the sample sites were extremely remote, samples were taken out intact, transferred to a cleaned plastic garbage can (rinsed with de-ionized water), weighed, and left to melt at room temperature. Where samples were a mixture of ice and water, the liquid portion was measured in the field. An aliquot was taken for chemical analyses, and the remainder was discarded. Chemical analysis of the bulk precipitation samples were conducted by the Illinois State Water Survey according to methods of Peden (1986).

2.2. Data Analytical Techniques

2.2.a. Lake Chemical Analyses

Five hundred sixty five individual samples were collected over the ten year period. Of these, 475 had complete analyses and were examined for ion percent difference (IPD) between measured positively and negatively charged ions. This is a common quality assurance procedure to determine the quality of individual samples. Total ionic strength (IS) for nearly all samples was greater than 200 µeq/L. According to standard QA procedures, maximum allowable IPD is 60% for samples where IS <50 µeq/L, 30% for samples where 50 ≤IPD<100 µeq/L, and 15% for samples with IPD ≥ 100 µeq/L (Stensland and Bowersox 1984, O'Deen et al. 1994). Twenty seven of the total samples failed to meet the 15% cutoff for acceptable IPD. These samples failed for a number of reasons. A few were obviously contaminated (extreme values for chloride, calcium, or sulfate), but most had either all cations or all anions lower than other, similar samples.

The 27 samples with IPD > 15% were eliminated from the data set. The 90 samples with incomplete analyses (missing alkalinities) were left in the data set. I arbitrarily removed all samples from lake hypolimnia, in order to use the most conservative and similar data set possible for comparing precipitation and surface water. Lake bottom waters can be influenced by biological activities in the sediments and I didn't want this possibility to complicate interpretation of the results. This left a total of 438 samples in the data base (Table 1).

Table 1. Number of samples and sample weeks remaining in data set after removal of hypolimnion samples and samples not meeting ion percent difference criteria.

LAKE	Sample Number	Number of Sample Weeks
Black Joe	90	32
Hobbs	90	33
Deep	83	30
Ross	90	27
Saddlebag	76	21
TOTALS	438	n/a

2.2.b. Change in Analytical Laboratories in 1991

Samples collected between 1984-1990 were analyzed by the USGS Central Analytical Laboratory in Arvada, CO. Samples from 1991-1993 were analyzed by the USFS Biogeoechemical Laboratory in Fort Collins CO. A Wilcoxon Rank Sum test, a nonparametric test for comparing two independent groups, was used to interpret whether bias had been introduced to the data set by the change in laboratories, since this is critical to interpreting whether trends had occurred in lake chemistry over time.

7

The Wilcoxon Rank Sum test was run for each lake separately, to eliminate the variance that would be introduced by combining lakes with different mean analyte concentrations.

The Wilcoxon Rank Sum test results had to be interpreted carefully. The probability that |Z| was greater than 0.01 indicated similar sample means. Values of |Z| less than 0.01 differed significantly, but this could be the result either of error introduced by the laboratory switch, or of real trends in lake chemistry. Using the Wilcoxon Rank Sum test results and visual inspection of the data over time, analytes were separated into three categories: (1) the analyte was categorized as biased by the laboratory change where Wilcoxon Rank Sum test and visual inspection of a time series plot of the data showed significant differences in analysis of a solute between laboratories for all lakes; (2) the analyte was categorized as unbiased by the laboratory change where Wilcoxon Rank Sum test showed no significant differences in analysis of a solute between laboratories; and (3) the time and concentration trends were individually interpreted where Wilcoxon Rank Sum test and visual inspection results were not clear-cut (Table 2a-e, Figure 2a-e).

Wilcoxon Rank Sum test statistics indicate that field pH and conductivity fell into the first category. Significant differences in the values for these analytes occurred at the time of the laboratory change. Examination into why this occurred revealed that field analyses for pH and conductivity were not available prior to 1991 and results reported are laboratory values. Sulfate was the only analyte that was not affected by the laboratory change. The remainder: calcium, magnesium, sodium, potassium,

Table 2a. Comparison of the mean analyte values from the USGS Central Analytical Laboratory (1984-1990) with those from the USFS Biogeochemistry Laboratory (1991-1993). Values after laboratory name are number of samples analyzed at each laboratory. All values except pH and specific conductance are in µeq/L. Specific conductance is reported as µS/cm^2. Asterisks after the IZI values represent significant differences in concentration between laboratories.

| LAKE AND ANALYTE | MEAN VALUE | | STANDARD DEVIATION | | |
	USGS (62)	USFS (28)	USGS	USFS	Prob>IZI
BLACK JOE LAKE pH	7.4	6.8	0.5	0.2	0.0001 *
specific conductance	15.1	13.6	1.9	1.8	0.0009 *
calcium	80.9	92.1	11.6	16.1	0.0009 *
magnesium	19.5	20.9	13.5	4.4	0.0054 *
sodium	19.4	22.9	4.5	3.9	0.0012 *
potassium	8.0	8.3	2.1	1.3	0.1461
ammonium	0.9	0.6	0.9	0.8	0.0041 *
chloride	7.3	5.3	2.7	1.1	0.0001 *
nitrate	0.5	5.9	0.6	5.6	0.0001 *
sulfate	30.9	33.1	7.8	5.7	0.0515
alkalinity	82.0	96.7	14.5	19.0	0.0005 *

Table 2b. Comparison of the mean analyte values from the USGS Central Analytical Laboratory (1984-1990) with those from the USFS Biogeochemistry Laboratory (1991-1993). Values after laboratory name are number of samples analyzed at each laboratory. All values except pH and specific conductance are in µeq/L. Specific conductance is reported as µS/cm². Asterisks after IZI represent significant differences between laboratories.

| LAKE AND ANALYTE | MEAN VALUE | | STANDARD DEVIATION | | Prob>IZI |
	USGS (54)	USFS (29)	USGS	USFS	
DEEP LAKE					
pH	7.5	6.7	0.5	0.2	0.0001 *
specific conductance	14.2	12.2	2.7	2.2	0.0001 *
calcium	82.5	89.8	16.0	19.7	0.0692
magnesium	11.9	13.6	4.4	2.4	0.0081 *
sodium	16.7	16.4	5.5	2.8	0.5951
potassium	5.8	5.9	1.3	1.0	0.4046
ammonium	0.9	0.3	1.3	0.6	0.0001 *
chloride	7.8	5.2	3.5	1.9	0.0001 *
nitrate	0.6	3.0	0.6	4.9	0.2820
sulfate	30.8	32.3	7.2	8.6	0.2605
alkalinity	73.9	81.8	13.9	16.1	0.0626

Table 2c. Comparison of the mean analyte values from the USGS Central Analytical Laboratory (1984-1990) with those from the USFS Biogeochemistry Laboratory (1991-1993). Values after laboratory name are number of samples analyzed at each laboratory. All values **except** pH and specific conductance are in µeq/L. Specific conductance is reported as µS/cm^2. Asterisks after IZI represent significant differences between laboratories.

| LAKE AND ANALYTE | MEAN VALUE | | STANDARD DEVIATION | | |
	USGS (67)	USFS (23)	USGS	USFS	Prob>IZI
HOBBS LAKE pH	7.3	6.8	0.5	0.2	0.0001 *
specific conductance	14.5	11.9	2.6	1.8	0.0001 *
calcium	82.1	82.0	15.5	15.5	0.9963
magnesium	19.5	20.3	4.3	4.1	0.3336
sodium	21.7	22.2	4.0	4.1	0.5310
potassium	6.4	5.3	1.7	0.8	0.0001 *
ammonium	0.7	0.7	0.5	1.4	0.0007 *
chloride	7.4	4.5	2.9	2.5	0.0001 *
nitrate	2.3	1.6	0.3	1.6	0.8283
sulfate	19.4	16.4	8.5	2.4	0.7918
alkalinity	91.3	97.6	22.3	19.9	0.1136

Table 2d. Comparison of the mean analyte values from the USGS Central Analytical Laboratory (1984-1990) with those from the USFS Biogeochemistry Laboratory (1991-1993). Values after laboratory name are number of samples analyzed at each laboratory. All values **except** pH and specific conductance are in µeq/L. Specific conductance is reported as µS/cm^2. Asterisks after |Z| represent significant differences between laboratories.

LAKE AND ANALYTE	MEAN VALUE		STANDARD DEVIATION		
	USGS (60)	USFS (30)	USGS	USFS	Prob>|Z|
ROSS LAKE pH	7.4	6.7	0.7	0.2	0.0001 *
specific conductance	11.9	10.0	1.8	101	0.0001 *
calcium	54.3	63.6	5.5	9.3	0.0001 *
magnesium	17.2	18.4	11.4	1.6	0.0001 *
sodium	19.6	20.3	4.3	5.4	0.5219
potassium	7.7	7.4	3.2	0.8	0.6929
ammonium	0.8	0.9	0.6	1.1	0.3858
chloride	7.2	7.9	2.2	3.8	0.2602
nitrate	0.5	6.0	0.8	15.5	0.0006 *
sulfate	19.7	20.4	3.2	2.4	0.0806
alkalinity	67.3	67.8	8.3	7.6	0.4266

Table 2e. Comparison of the mean analyte values from the USGS Central Analytical Laboratory (1984-1990) with those from the USFS Biogeochemistry Laboratory (1991-1993). Values after laboratory name are number of samples analyzed at each laboratory. All values except pH and specific conductance are in µeq/L. Specific conductance is reported as µS/cm^2. Asterisks after IZI represent significant differences between laboratories.

| LAKE AND ANALYTE	MEAN VALUE		STANDARD DEVIATION		
	USGS (48)	USFS (28)	USGS	USFS	Prob>IZI
SADDLEBAG LAKE pH	7.3	6.6	0.6	0.2	0.0001 *
specific conductance	12.1	10.6	1.3	1.8	0.0001 *
calcium	56.5	63.3	6.8	9.8	0.0036 *
magnesium	14.1	15.4	3.8	2.4	0.0923
sodium	25.3	22.9	8.0	4.1	0.4825
potassium	7.0	6.8	1.4	1.4	0.3207
ammonium	0.9	1.4	0.5	1.7	0.9871
chloride	5.9	6.2	1.0	1.8	0.4883
nitrate	0.6	6.7	0.6	5.9	0.0001 *
sulfate	22.4	22.4	2.8	2.4	0.7211
alkalinity	76.7	66.1	4.4	15.3	0.0124

Figure 2. Mean concentrations of lake water solutes over time for a) Black Joe Lake; b) Deep Lake; c) Hobbs Lake; d) Ross Lake; and e) Saddlebag Lake. Mean values were calculated for all sites except hypolimnion at a lake by sample date. All solutes except pH are in μeq/L. pH is reported in pH units.
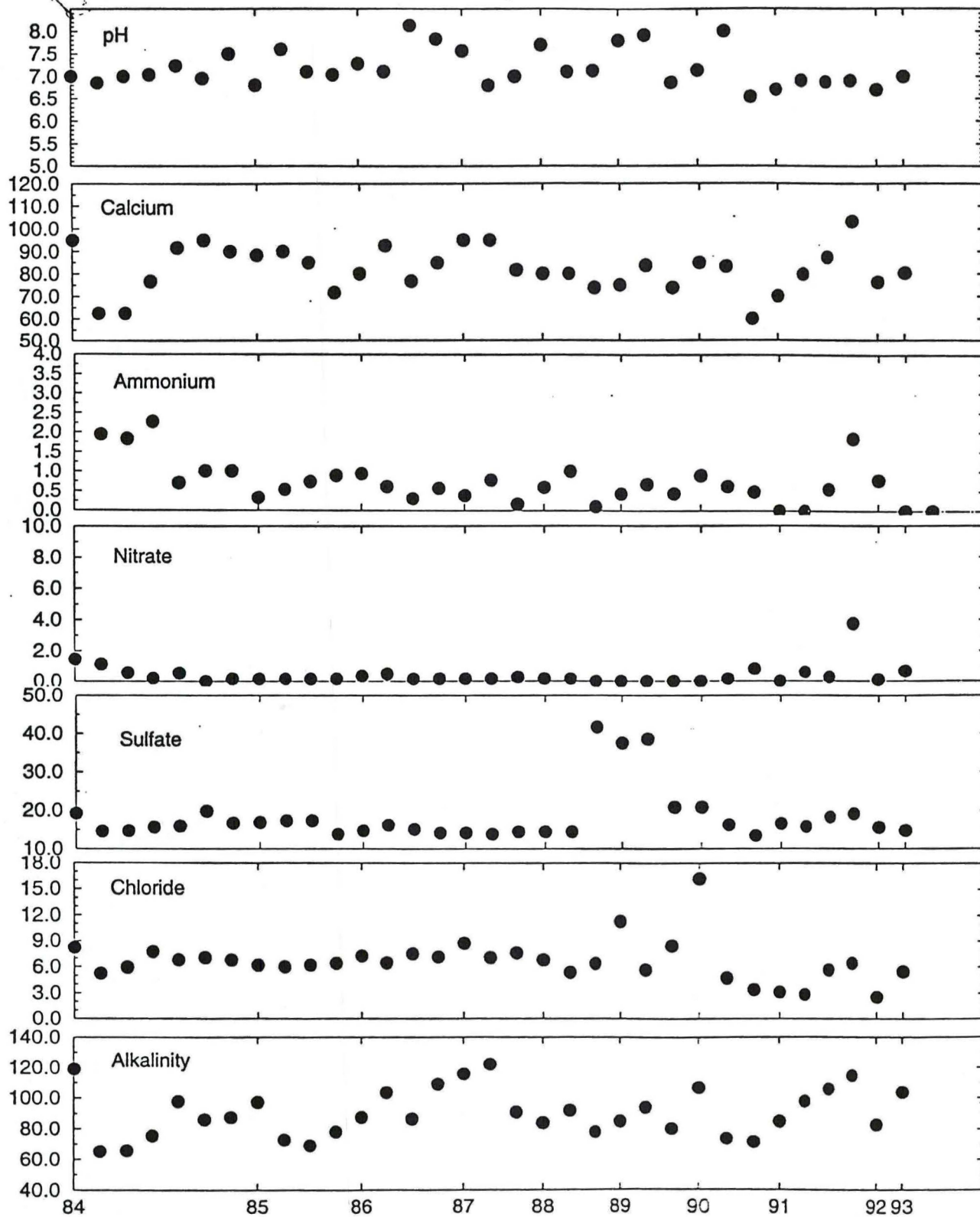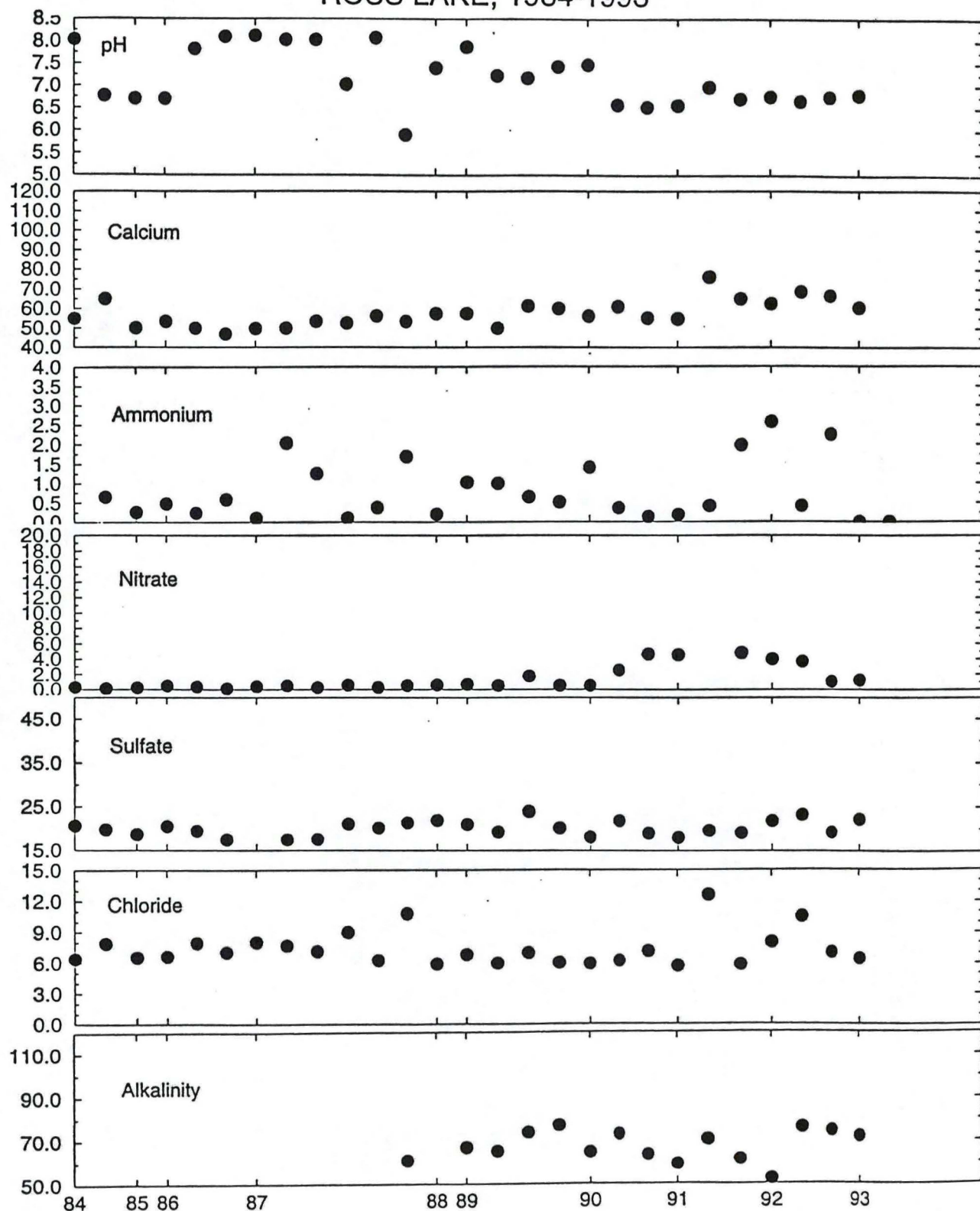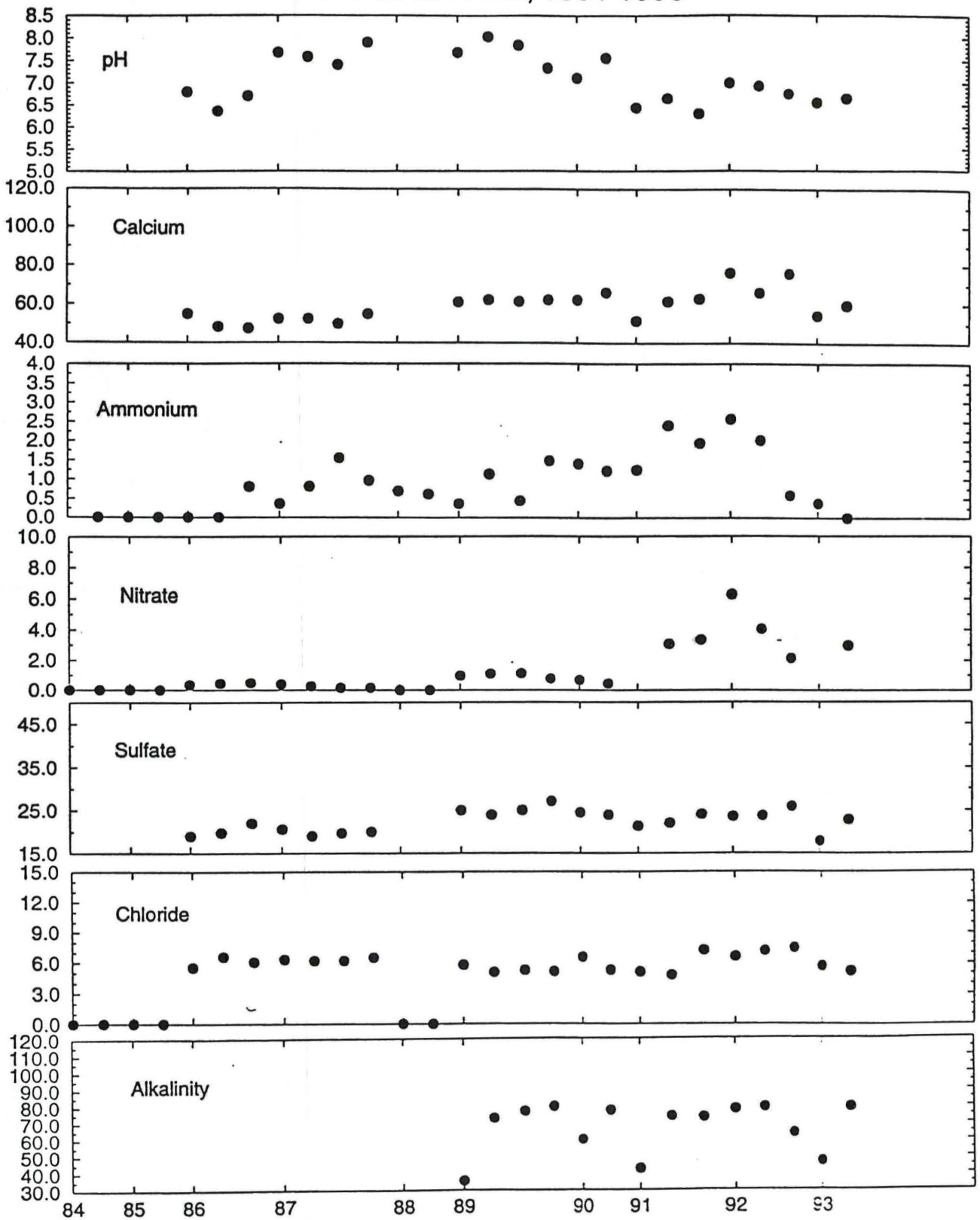
BLACK JOE 1984-1993

DEEP LAKE, 1984-1993

pH

Calcium

Ammonium

Nitrate

Sulfate
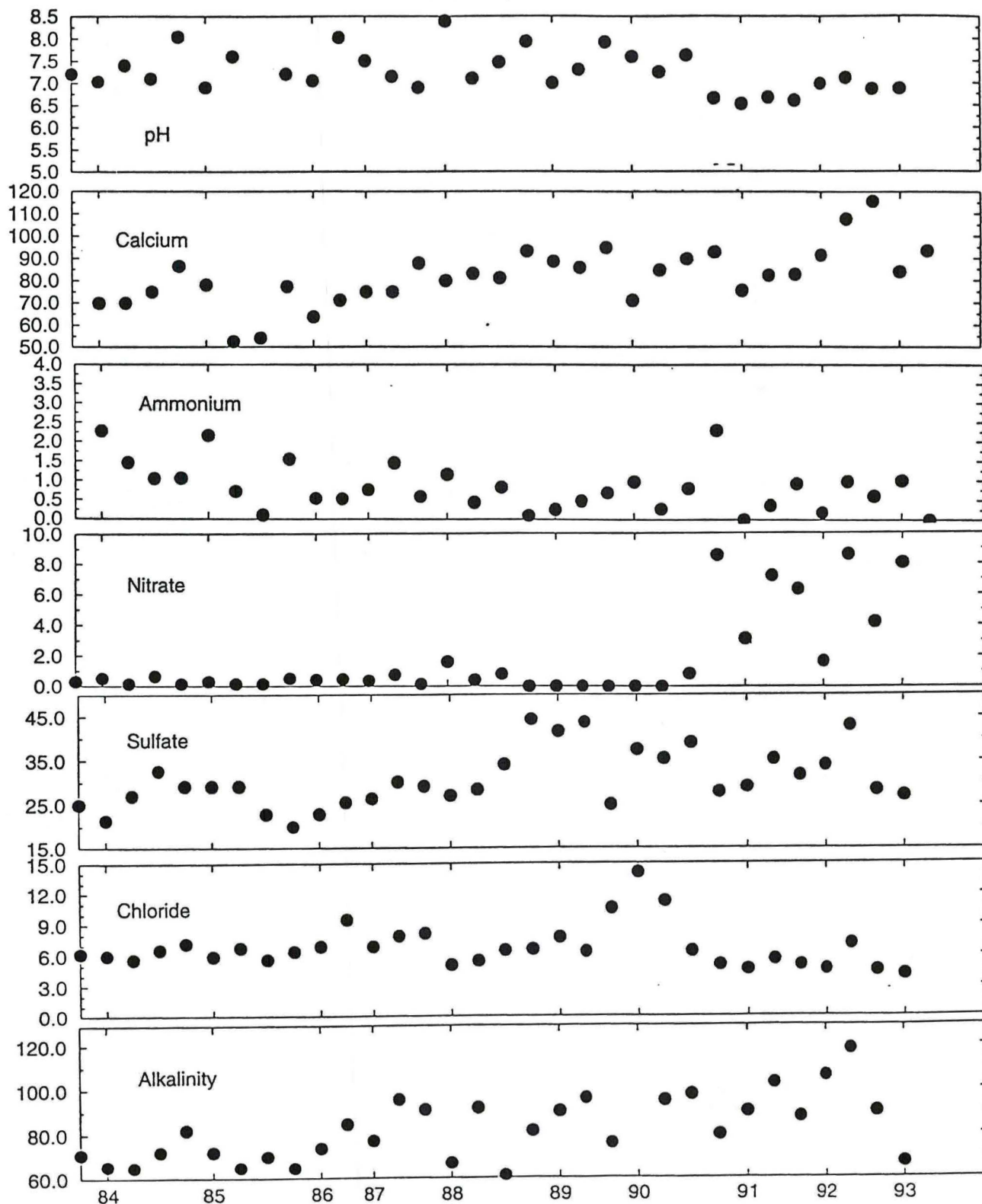
Chloride
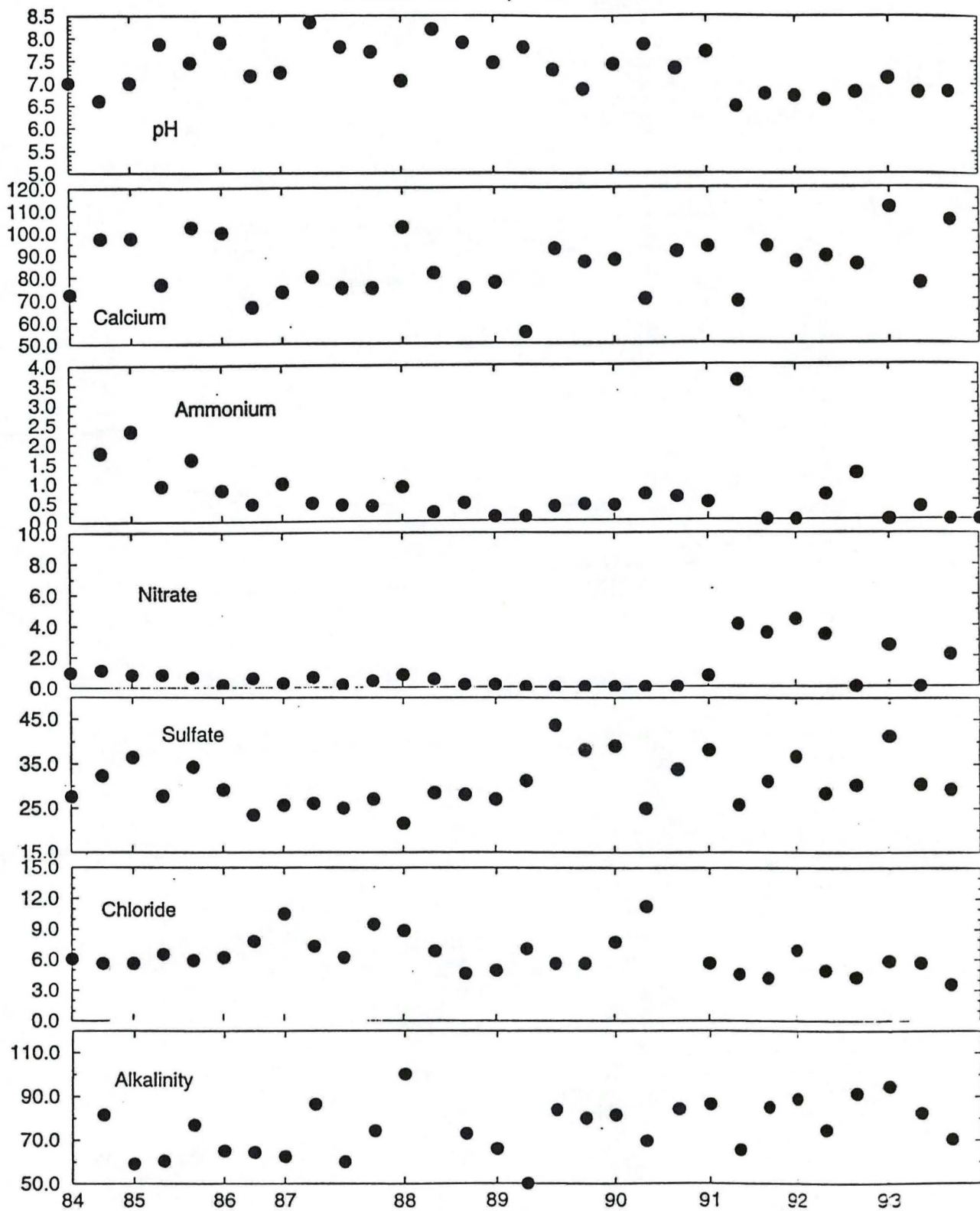
Alkalinity

HOBBS LAKE, 1984-1993

ROSS LAKE, 1984-1993

SADDLEBAG LAKE, 1984-1993

ammonium, chloride, nitrate, and alkalinity, differed significantly for some, but not all, lakes. These analytes were interpreted individually.

3.0 RESULTS

3.1. Lake Chemistry

The Wind River lakes are very dilute, as can be seen from the mean concentrations of major solutes (Table 3). Calcium was the most abundant cation in all the lakes; ANC and sulfate were the dominant anions. Ross and Saddlebag Lakes, the two lakes on the eastern side of the Wind Rivers, were more dilute overall, but showed slightly higher concentrations of ammonium, nitrate, and chloride, than western side lakes. Hobbs Lake had the lowest mean nitrate and sulfate values. Black Joe, Deep, and Saddlebag Lakes are the most southerly of the lakes. There was no distinction between these lakes in the south, and Hobbs and Ross Lake further north.

Time plots of analytes in each lake show some interesting differences between lakes (Figure 2a-e). Note the highly variable chemical dynamics for calcium, nitrate, sulfate, and chloride in Black Joe and Deep Lakes, and less variability in Saddlebag and Ross Lakes. Hobbs Lake had intermediate variability in solute concentrations.

Field analyses of pH and conductivity are thought to give more realistic assessment of these parameters, because field analysis minimizes the time unfiltered water sits in sample bottles where particulates can dissolve in or out of solution and where biological activity can affect water nutrient contents (Bigelow et al. 1989). For

20

Table 3. Summary of a) chemical and b) physical characteristics of the five Wind River study lakes. Values for chemical analytes represent means (and standard deviations) of annual means for surface, inlet, and outlet samples only collected from 1991-1993. Specific conductance (cond.) is shown as $\mu S/cm^2$, pH is in pH units, and all other solutes are as $\mu eq/L$.

a).

Lake	pH	cond.	Ca	Mg	Na	K	NH₄	Cl	NO₃	SO₄	ANC
Black Joe	6.8 (0.2)	13.6 (1.8)	92.1 (16.1)	20.9 (4.4)	22.9 (3.9)	8.3 (1.3)	0.6 (0.8)	5.3 (1.1)	5.9 (5.6)	33.1 (5.7)	96.7 (19.0)
Deep	6.7 (0.2)	12.2 (2.2)	89.9 (19.7)	13.6 (2.4)	16.4 (2.8)	5.9 (1.0)	0.3 (0.6)	5.2 (1.9)	3.0 (4.9)	32.3 (8.6)	81.8 (16.1)
Hobbs	6.8 (0.2)	11.9 (1.8)	82.0 (15.5)	20.3 (4.1)	22.2 (4.1)	5.3 (0.8)	0.7 (1.4)	4.5 (2.5)	1.6 (1.6)	16.4 (2.4)	97.6 (19.9)
Ross	6.7 (0.2)	10.0 (10.1)	63.6 (9.3)	18.4 (1.6)	20.3 (5.4)	7.4 (0.8)	0.9 (1.1)	7.9 (3.8)	6.0 (15.5)	20.4 (2.4)	67.8 (7.6)
Saddlebag	6.6 (0.2)	10.6 (1.8)	63.3 (9.8)	15.4 (2.4)	22.9 (4.1)	6.8 (1.4)	1.4 (1.7)	6.2 (1.8)	6.7 (5.9)	22.4 (2.4)	66.1 (15.3)

b).

Lake	Elevation (m)	Maximum Depth (m)	Surface Area (ha)	Watershed Area (ha)
Black Joe	3122	25.9	31	1036
Deep	3201	33.2	25	253
Hobbs	3085	17.4	8	389
Ross	2948	81.0	190	4494
Saddlebag	3432	22.5	17	185

this reason, I chose to use field values from post-1991 for interpretation of lake water quality (Figure 2a-e, Table 2a-e).

Nitrate shows dramatic changes before and after the laboratory change, but where the change was statistically different in Black Joe, Ross, and Saddlebag Lakes, it was not significant in Deep and Hobbs Lakes. The lack of significance in Deep and Hobbs Lakes is due to the increased variance in samples after 1991. The consistently low concentrations from analyses by the USGS laboratory confound interpretation of whether the difference in nitrate with time is an artifact of sample collection or analysis procedures, or represents a real increase in nitrate concentrations of surface waters.

Ammonium showed significant differences between sample laboratories for Black Joe Lake, but also for Deep and Hobbs Lakes, lakes that did not exhibit significant differences in nitrate concentrations. Ammonium concentrations, at 0.3-1.4 μeq/L, were very low, and any real increase or decrease in ammonium concentrations with time was too low to detect.

Calcium concentrations increased significantly in Black Joe (an increase of 11.2 μeq/L), Ross (an increase of 9.3 μeq/L), and Saddlebag (an increase of 6.8 μeq/L) Lakes. An increase of 7.3 μeq/L in Deep Lake was not significant, nor was a decrease of 0.1 μeq/L in Hobbs Lake. Other base cations changed slightly, with magnesium showing a slight increase in all five lakes pre- and post-1991, and sodium and potassium both increasing and decreasing slightly in different lakes.

Sulfate concentrations did not change significantly in the lake samples from 1984 to 1994. This implies analytical techniques at both the USGS and USFS

laboratories yielded similar sulfate concentrations, and also, that these concentrations did not change with time.

Chloride differs significantly before and after the laboratory change in the western lakes, Hobbs, Black Joe, and Deep Lakes. The values after 1991 are statistically lower than those before that date, but it is unclear whether this is because of laboratory changes or real chemical shifts in lake concentration. All three lakes had a few anomalously high chloride values reported prior to 1991; these are possibly results of sample contamination, and may have affected the Wilcoxon Rank Sum test results. When the outlier values were removed the |Z| became insignificant. The USGS chloride values had a positive bias of approximately 2 μeq/L for part of the record due to laboratory analytical error, and this may have influenced the statistics (Turk, personal communication).

The |Z| values for Black Joe Lake indicated significant differences in alkalinity concentrations coincident with the laboratory shift, but time plots for alkalinity suggest the difference may not be due to laboratory bias. For Black Joe Lake the time plot suggested alkalinity increased since 1984, and the Wilcoxon Rank Sum test results may reflect real surface water changes. Alkalinity for Deep, Hobbs, and Ross Lakes increased with time, but values were not significantly different before and after 1991. Alkalinity declined slightly in Saddlebag Lake.

3.2. Deposition

Deposition is a product of both precipitation concentration and precipitation amount. Concentrations and precipitation amounts for four sites surrounding the Wind

Rivers may be good estimates of regional chemistry in areas of low relief, but concentrations at lower elevation may or may not be good estimates of concentrations at higher elevations (Warren et al. 1991, Baron and Denning 1993). It is difficult to quantify precipitation amount at high elevations due to difficulty of access, but it may also be invalid to calculate deposition at high elevations from low elevation data due to complex meteorology (Baron and Denning, 1993, Parrish et al. 1990). In Section 3.2 below, deposition to the high elevations of the Wind Rivers is estimated a number of different ways. First, NADP concentration and deposition data from the four sites surrounding the Wind Rivers are presented. Second, NADP concentration data are extrapolated to high elevations using precipitation isopleths developed by the Soil Conservation Service (now Natural Resources Conservation Service). Third, bulk deposition measured at high elevations is presented, and finally, the concentrations from the bulk collectors are paired with the precipitation isopleths.

3.2.a. NADP Deposition

The four NADP sites surrounding the Wind Rivers showed similar patterns of precipitation and solute deposition. The occurrence of wet and dry years was regional; for instance, 1987 and 1993 were wet years at all four sites, while 1988 was a dry year (Figure 3a). Mean precipitation ranged 30-42 cm, and the two southern-most sites, Sinks Canyon and South Pass City, were wetter than the other two sites. Winter totals were similar among all four sites, but the spring, summer and fall precipitation amounts were higher at Sinks Canyon and South Pass City (Table 4).

24

Figure 3. Annual a) precipitation (in cm); b) calcium; c) sulfate; d) nitrate deposition (in kg/ha) for four NADP/NTN sites located around the Wind River Mountains. Refer to Figure 1 for location of sites.

Precipitation
1984-1994

Calcium Deposition
1984-1994

Sulfate Deposition
1984-1994

Nitrate Deposition
1984-1994

Year
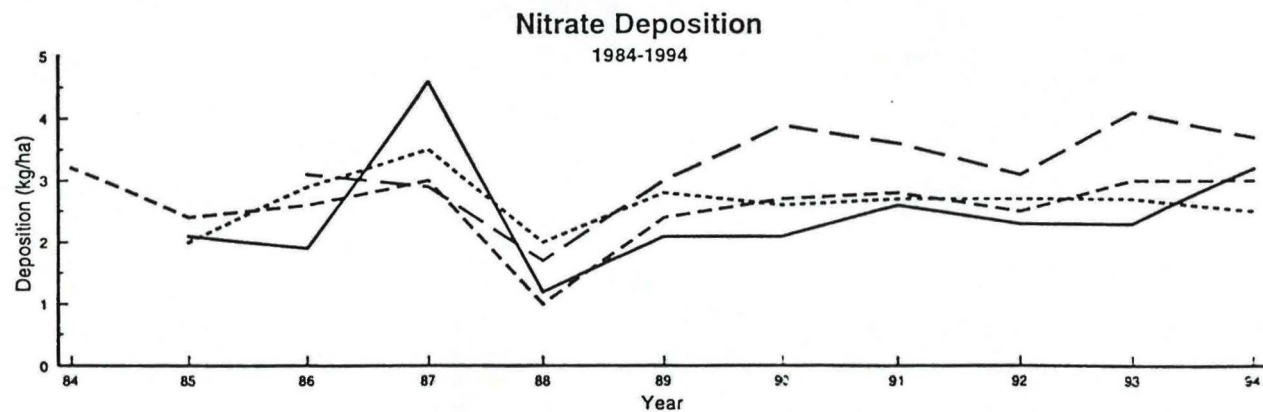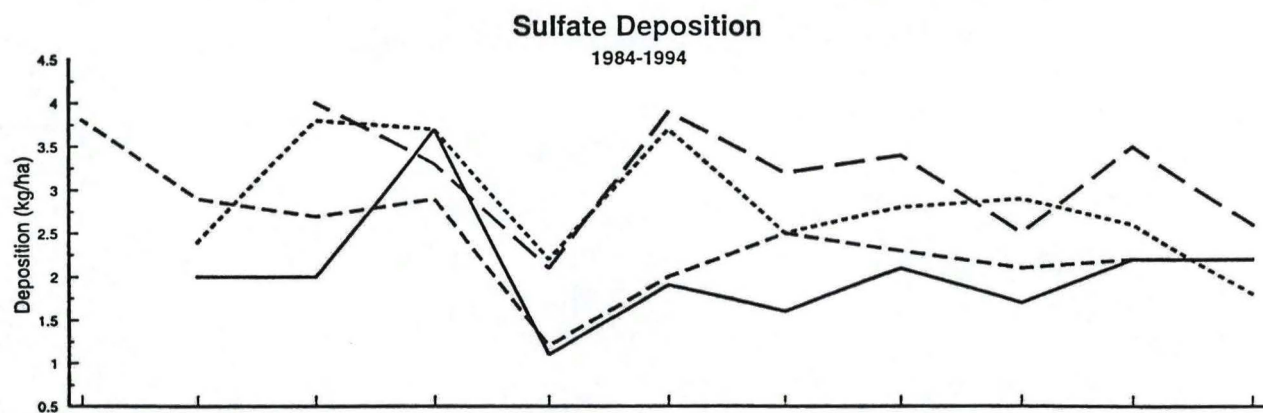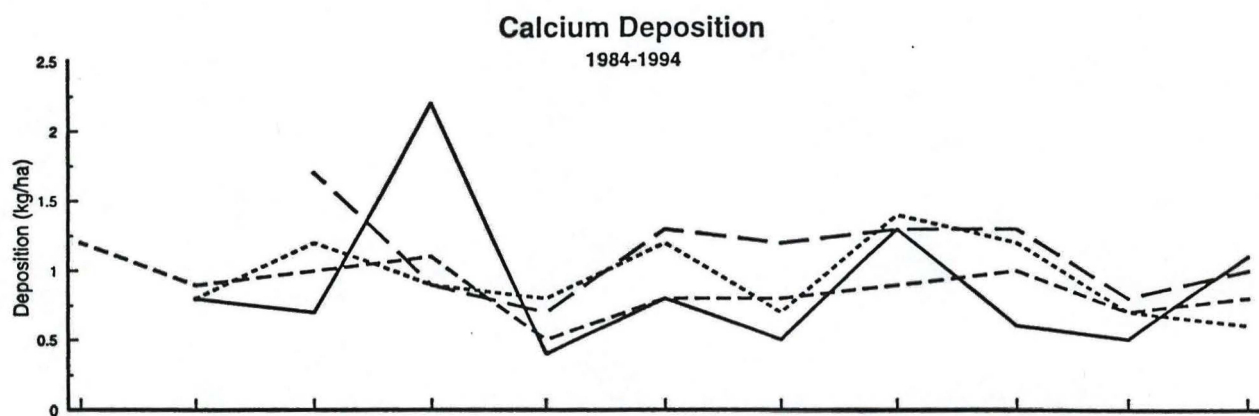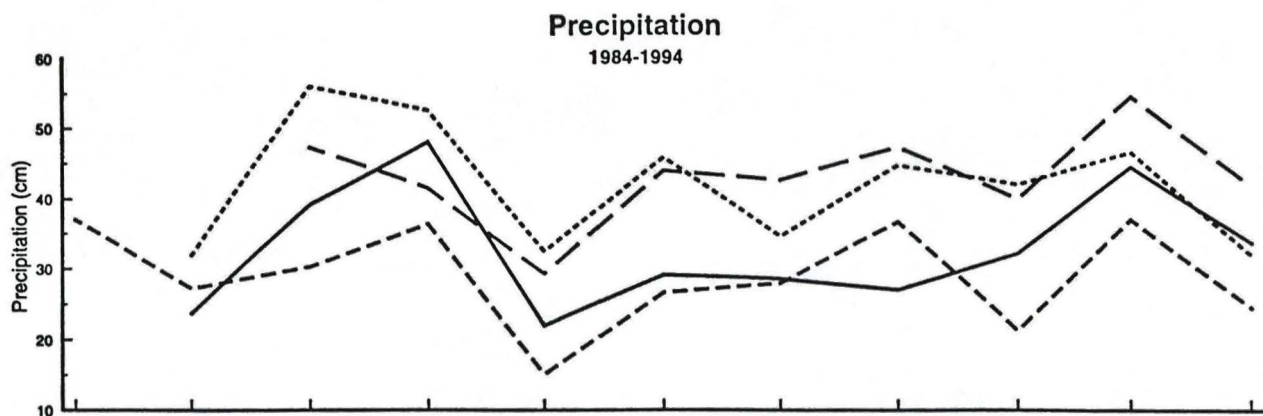
Gypsum Creek (WY98) Pinedale (WY06) Sinks Canyon (WY02) S. Pass City (WY97)

Table 4. Annual and seasonal precipitation patterns at four Wyoming National Atmospheric Deposition Program sites surrounding the Wind River Mountains. Winter, as defined by NADP, is December-February, spring is March-May, summer is June-August, and fall is September-November. Results are averages (and standard deviations) of the years 1986-1994, in cm.

SITE	ANNUAL	WINTER	SPRING	SUMMER	FALL
Pinedale	28.4 (7.2)	3.8	8.0	9.0	7.1
Gypsum Creek	33.8 (8.1)	6.3	8.8	9.5	8.5
Sinks Canyon	43.0 (8.1)	5.3	15.8	10.3	11.6
South Pass City	43.2 (6.5)	9.4	14.6	8.8	9.9

Sulfate concentrations were slightly greater than nitrate concentrations at all sites, and pH, at 5.2-5.3, was fairly high (Table 5). Nitrate and sulfate were more concentrated at Pinedale, but so were all other solutes, including base cations and ammonium.

Trend histories in precipitation concentrations for the Wyoming NADP sites reveal some significant changes from 1985 through 1993 for Pinedale, Sinks Canyon, and Gypsum Creek (Table 6; Lynch et al. 1995a). Observed and predicted (from least squares general linear model regression) trends in concentration data are reprinted from Lynch et al. (1995a) in Figure 4 for Sinks Canyon, Gypsum Creek, Pinedale, and South Pass City. Sulfate concentrations decreased by 24% at Gypsum Creek and 34% at Sinks Canyon between 1985 and 1993; the drop was significant at Sinks Canyon. There was an insignificant increase of 3% in sulfate concentrations at Pinedale. Nitrate concentrations increased by 8% at Sinks Canyon, 10% at Gypsum Creek, and 28% at Pinedale, however, none of these trends was significant. Acidity

Table 5. Volume-weighted mean precipitation chemistry (µeq/L) from four NADP wet deposition sites surrounding the Wind River Mountains. Field pH and conductivity values are measured at the field laboratories near the site of the collectors. Laboratory values are measured at the Central Analytical Laboratory in Illinois. Values are means of calendar years 1986-1994.

| ANALYTE	PINEDALE	GYPSUM CREEK	SINKS CANYON	SOUTH PASS CITY
pH (field)	4.8	4.9	4.9	4.9
pH (laboratory)	5.2	5.3	5.3	5.2
specific conductance (field)	11.6	8.1	8.2	9.1
specific conductance (laboratory)	7.3	6.4	6.1	7.1
calcium	14.5	13.0	11.5	13.0
magnesium	2.5	4.1	2.5	2.5
sodium	4.8	1.5	3.5	5.2
potassium	1.0	1.3	0.5	0.5
ammonium	10.0	11.6	7.8	6.1
chloride	4.8	3.9	2.5	3.7
nitrate	14.5	11.8	10.0	12.4
sulfate	16.3	12.5	13.5	15.4

Table 6. Trends in concentration (μeq/L) of individual ions in precipitation at three Wyoming NADP/NTN sites from 1985 through 1993. Data are from Lynch et al. (1995a) and were calculated using a two-stage, least squares general linear regression. *p < 0.05.

|	H	SO$_4$	NO$_3$	NH$_4$	Ca	Mg	K	Na	Cl
Sinks Canyon									
Change (μeq/L)	-2.76*	-5.06*	0.74	0.77	-3.93*	-1.45*	-0.18*	-0.13	-1.63*
Percent Change	-40.04	-33.97	8.43	12.89	-38.39	-50.52	-40.31	-5.63	-51.20
Gypsum Creek									
Change (μeq/L)	-3.42*	-3.23	1.03	3.19	-3.69	-0.73	-0.02	-0.21	-0.56
Percent Change	-52.97	-24.49	10.42	75.79	-33.02	-29.86	-3.06	-5.75	-14.88
Pinedale									
Change (μeq/L)	0.03	0.41	2.65	3.06	-1.33	-0.65	0.07	0.09	-0.11
Percent Change	0.67	3.43	27.74	62.86	-14.22	-28.6	22.95	2.42	-3.75

Figure 4. Observed and predicted ionic concentrations over time of major solutes in precipitation at four NADP sites surrounding the Wind River Mountains: Sinks Canyon (WY02), Gypsum Creek (WY98), Pinedale (WY06), and South Pass City (WY97). Figures are from Lynch et al. (1995a). Dots are seasonal volume-weighted mean concentrations. The solid lines are estimates from linear least squares regression of concentrations that incorporates both seasonal and long-term trends effects. The dashed line represents the LOWESS regression of observed bi-monthly data against time. LOWESS is a smoothing method that can depic non-linearities in trends, and while it provides a visual model for these graphs, was not used to statistically assess concentration trends (Lynch et al. 1995a).
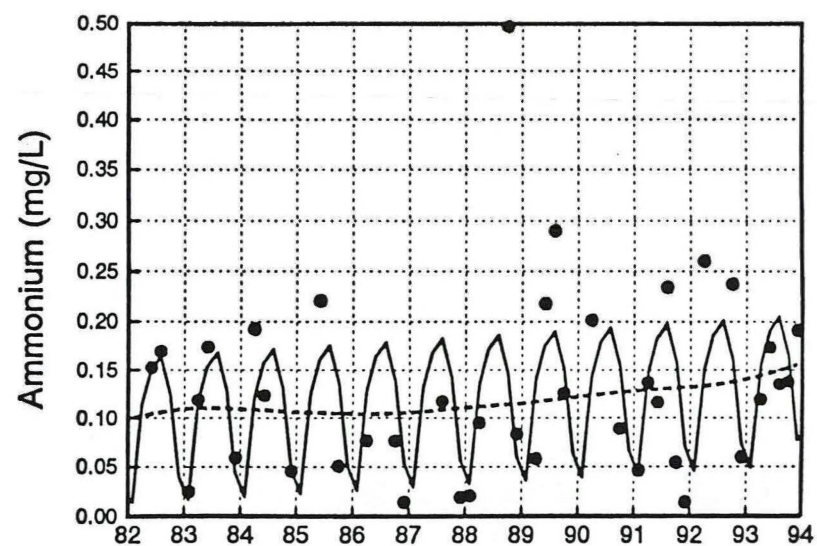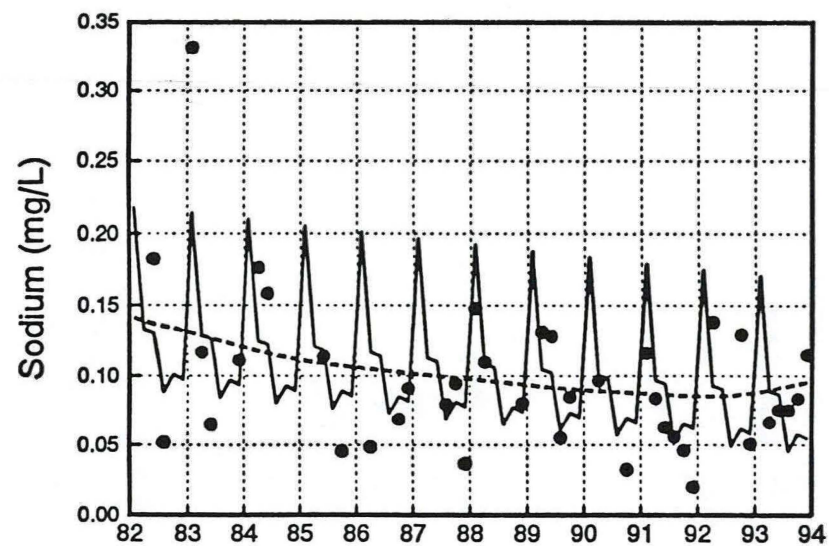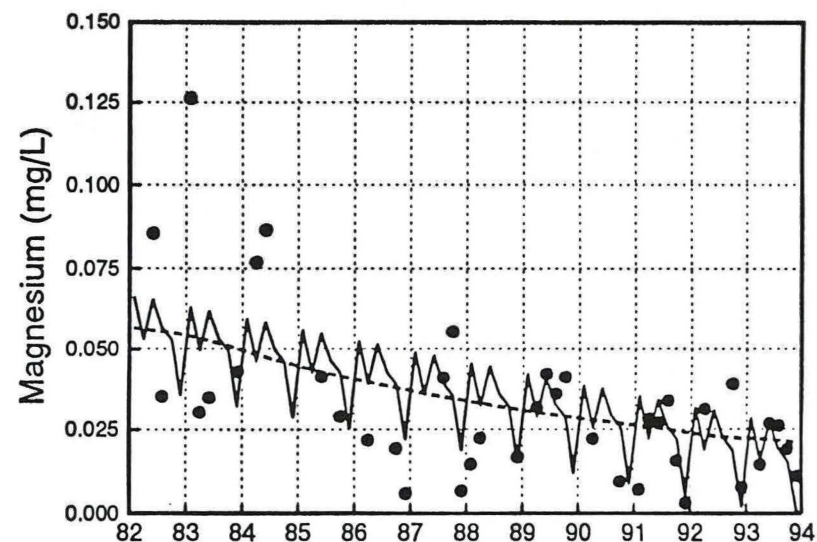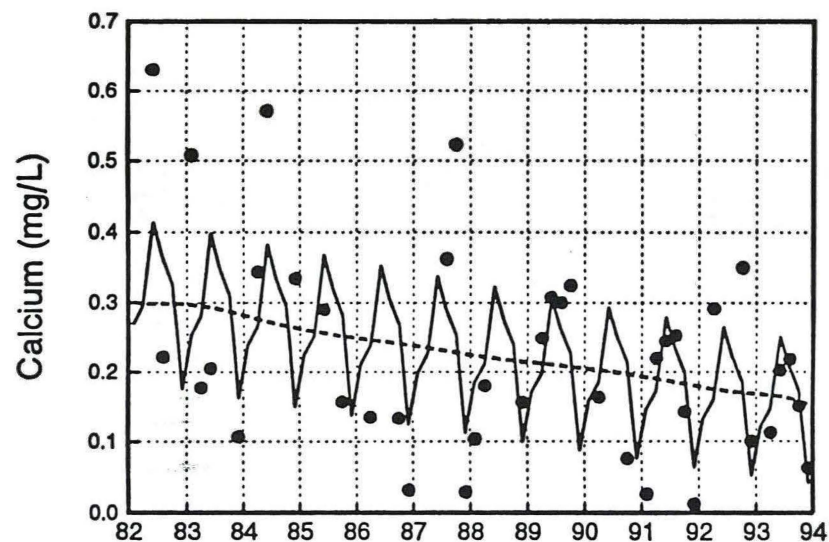
WY02 - Sinks Canyon
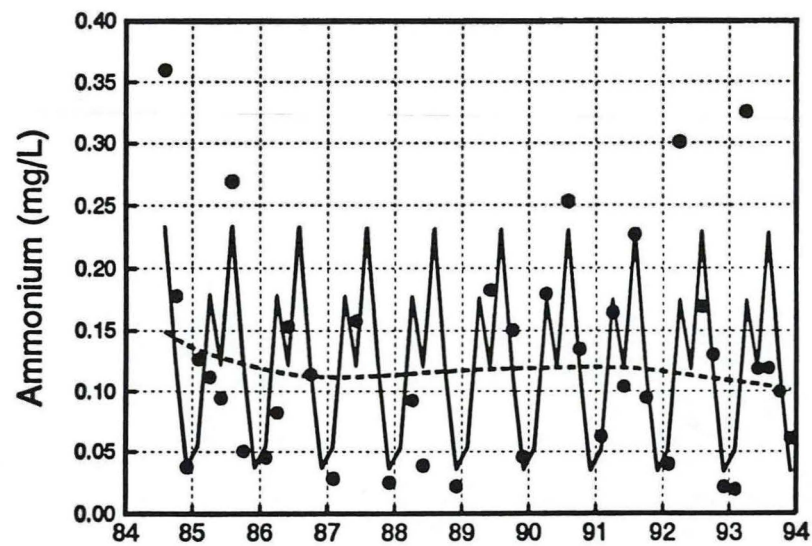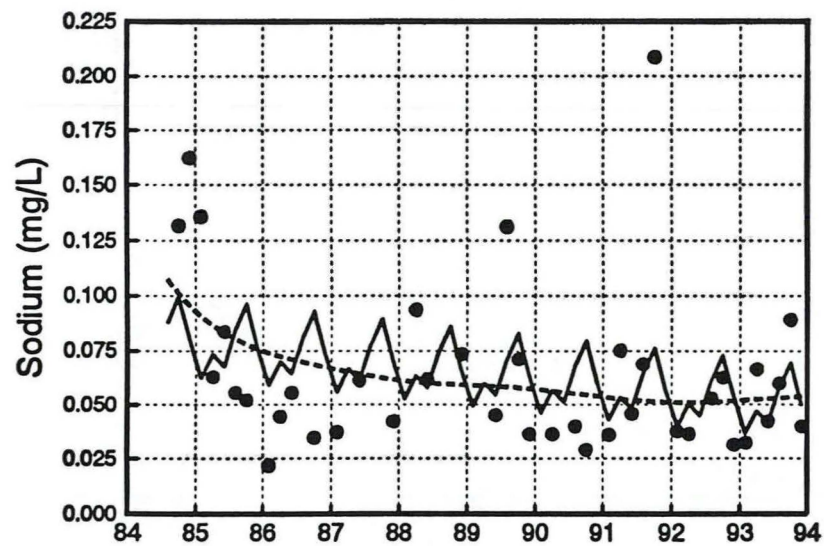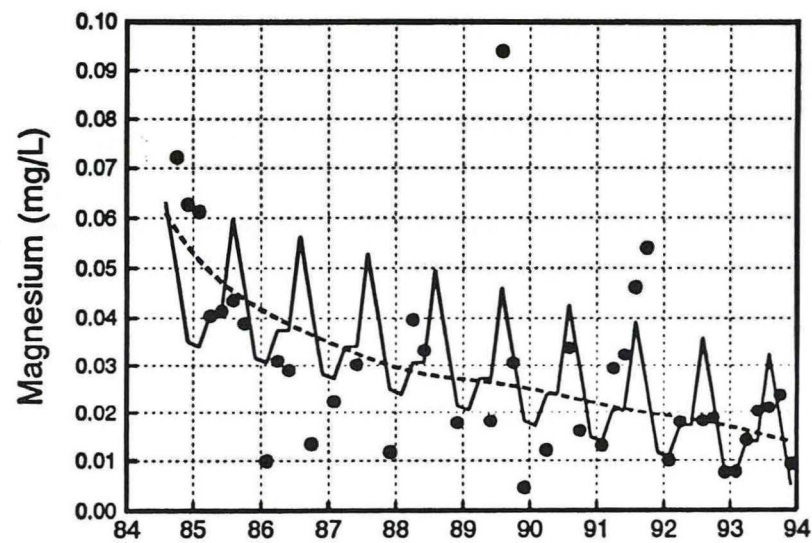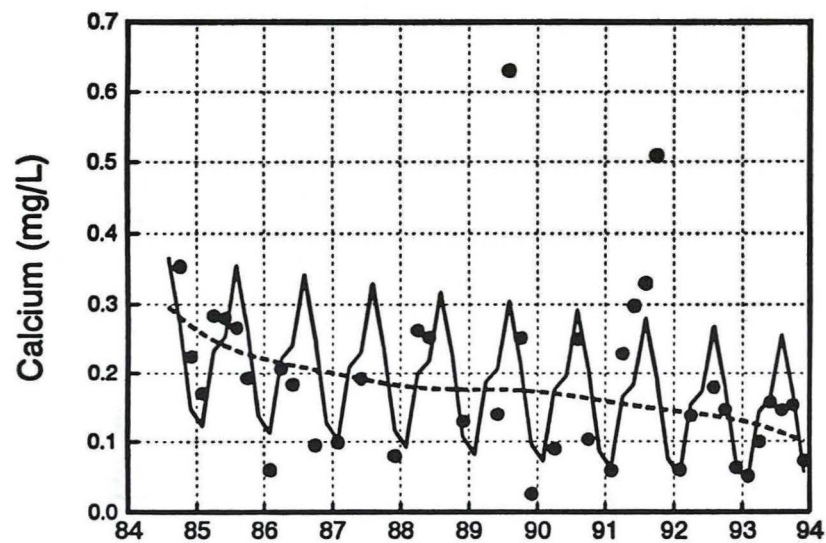
WY02 - Sinks Canyon
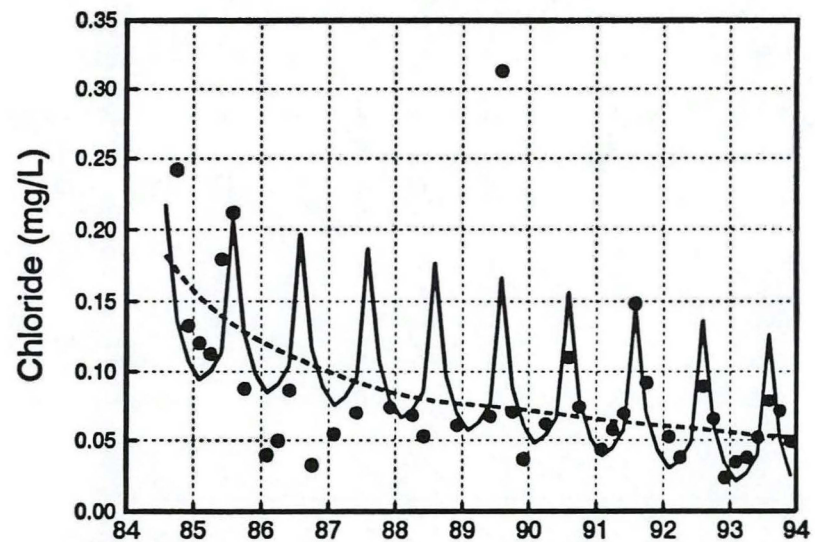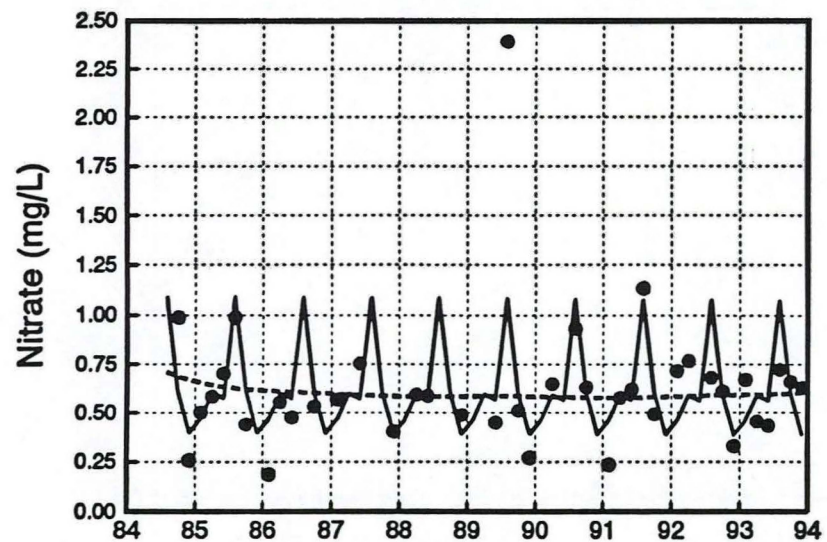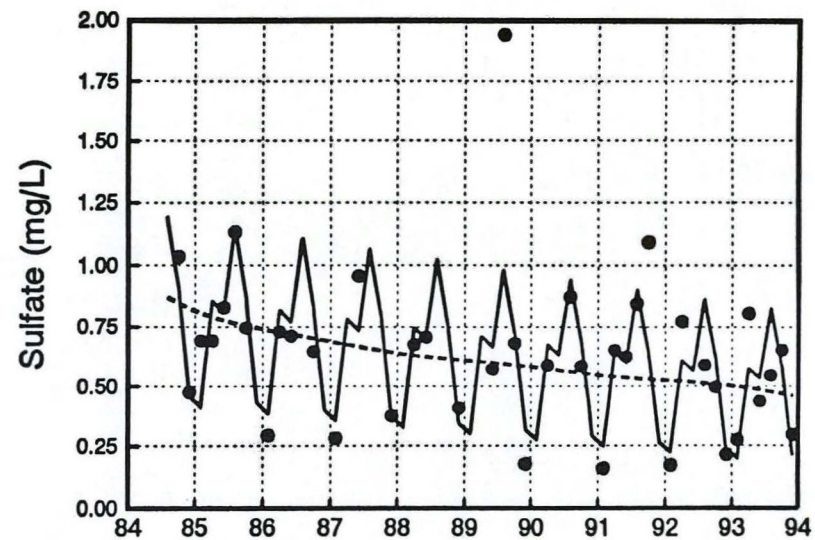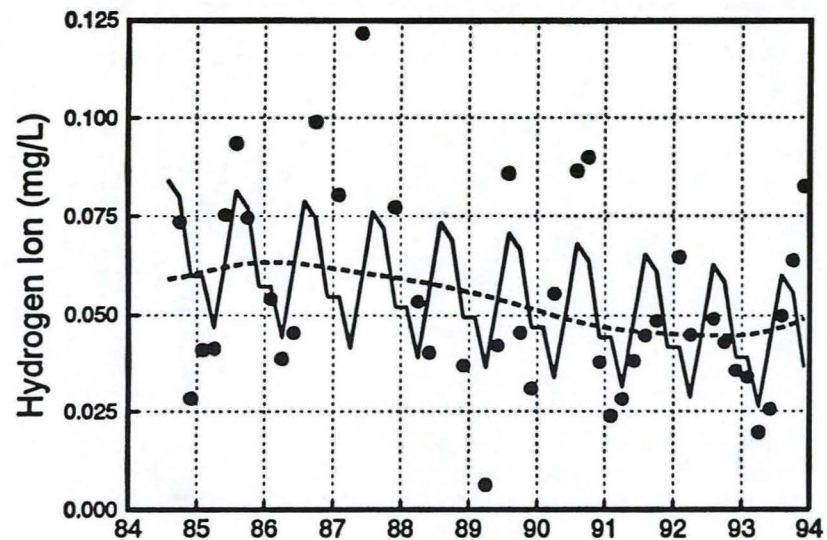
WY06 - Pinedale

WY06 - Pinedale
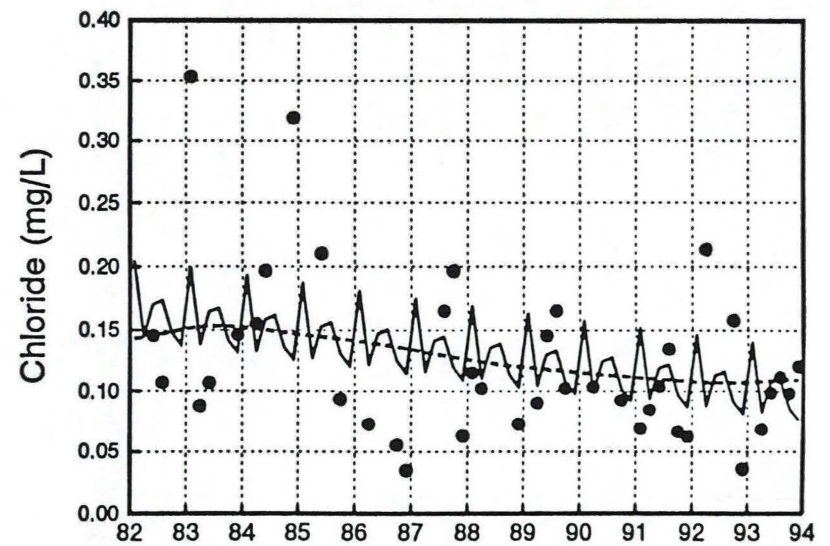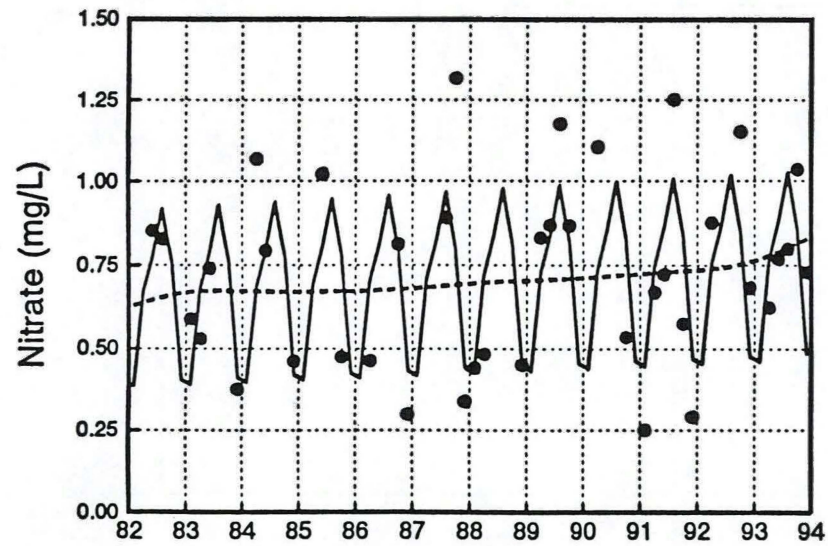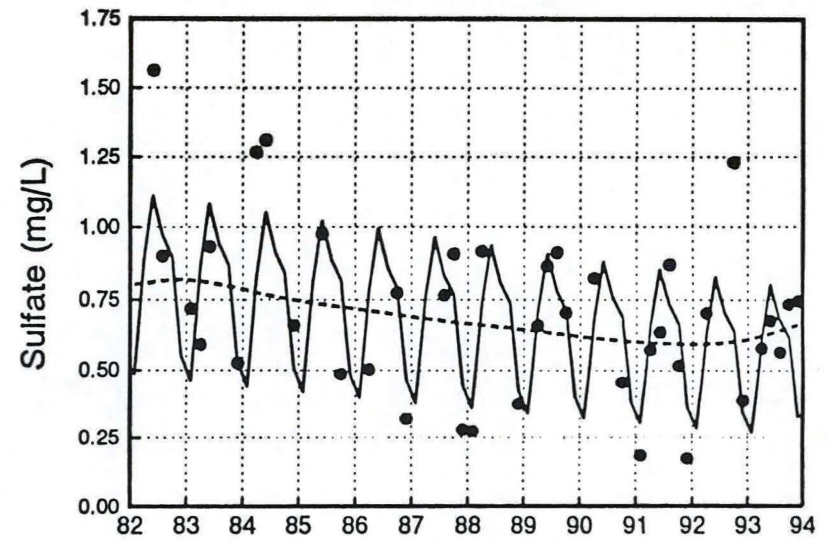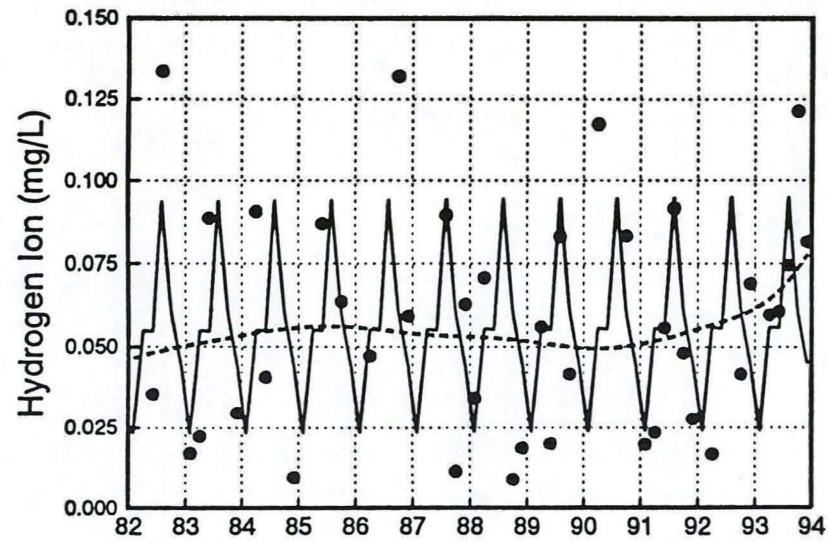
WY97 - South Pass City
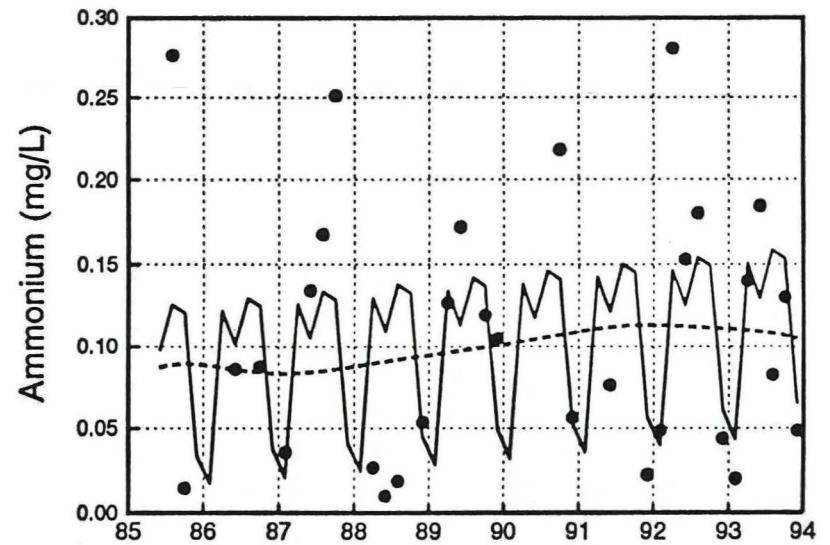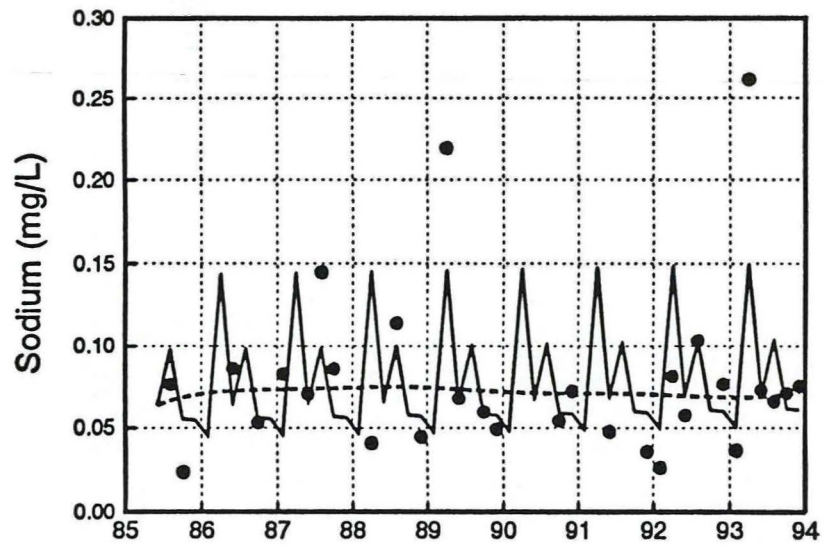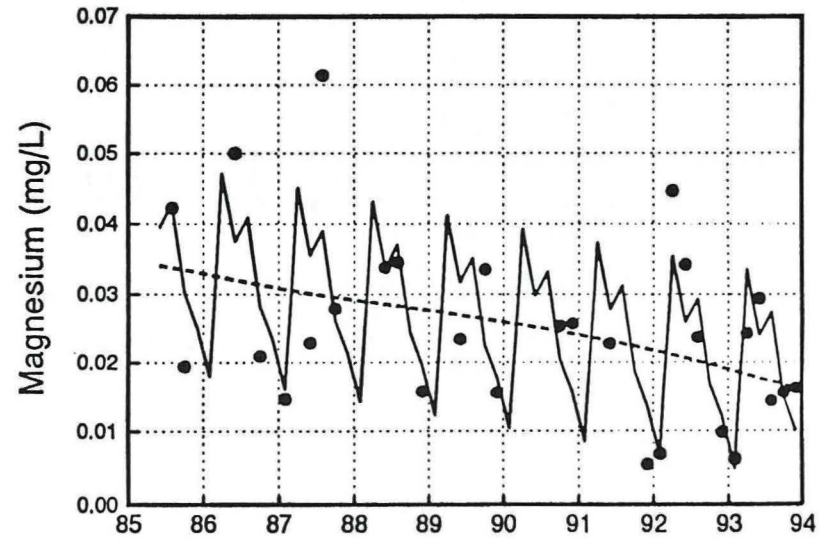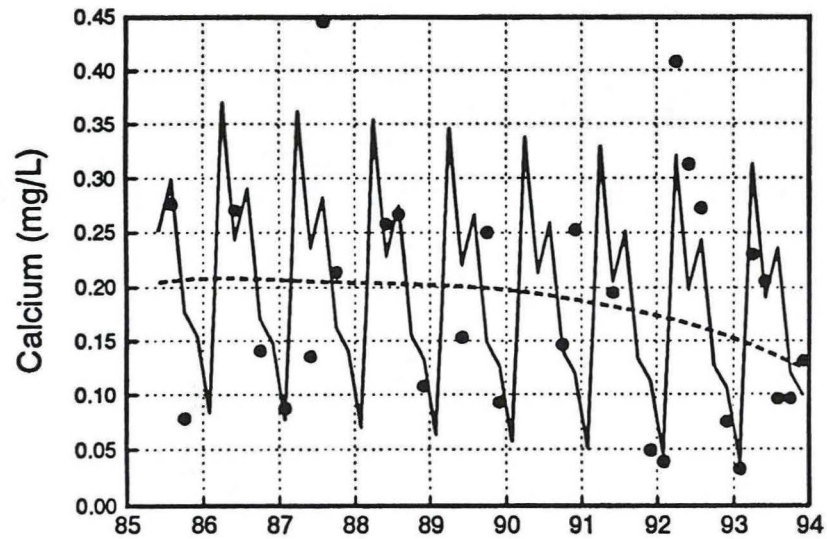
WY97 - South Pass City
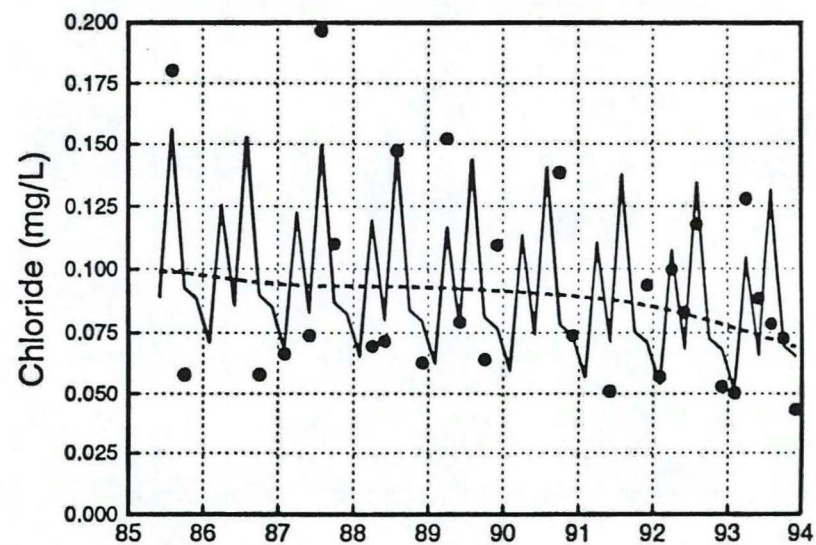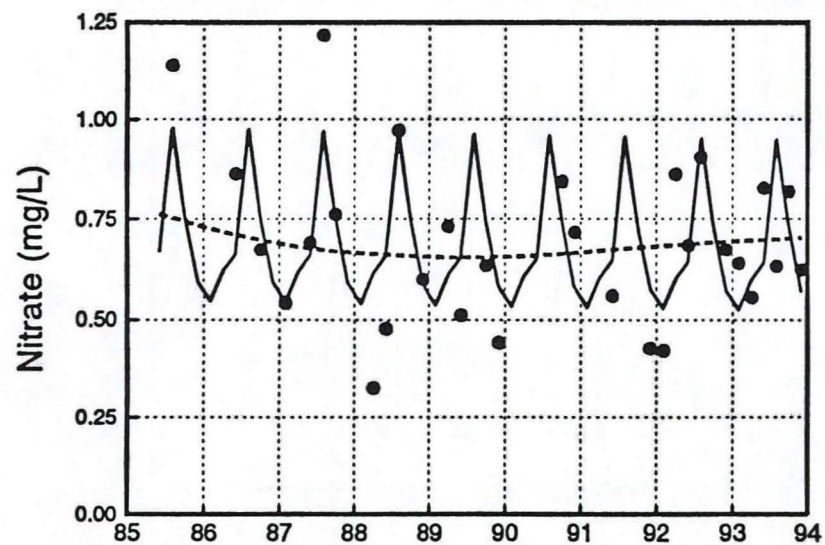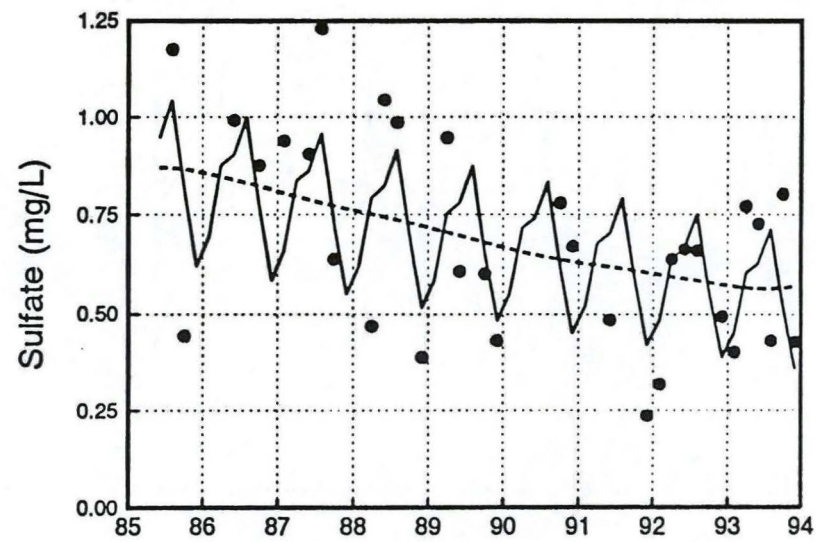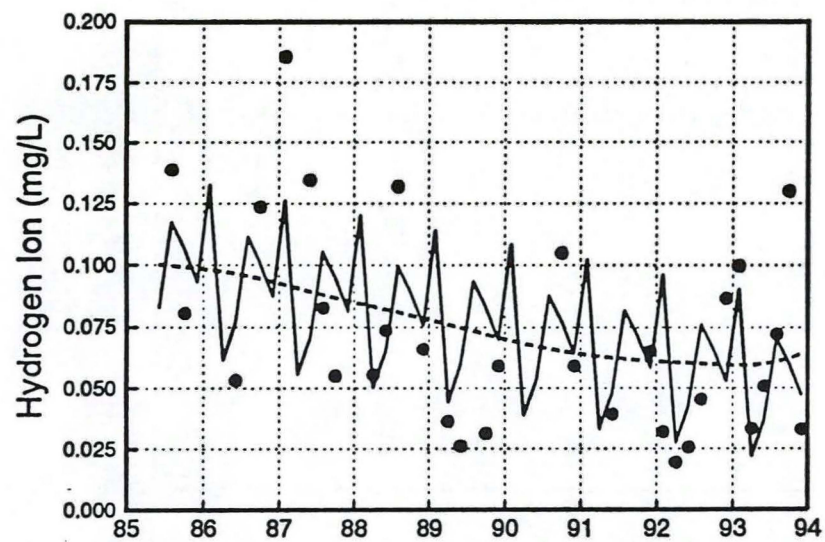
WY98 - Gypsum Creek
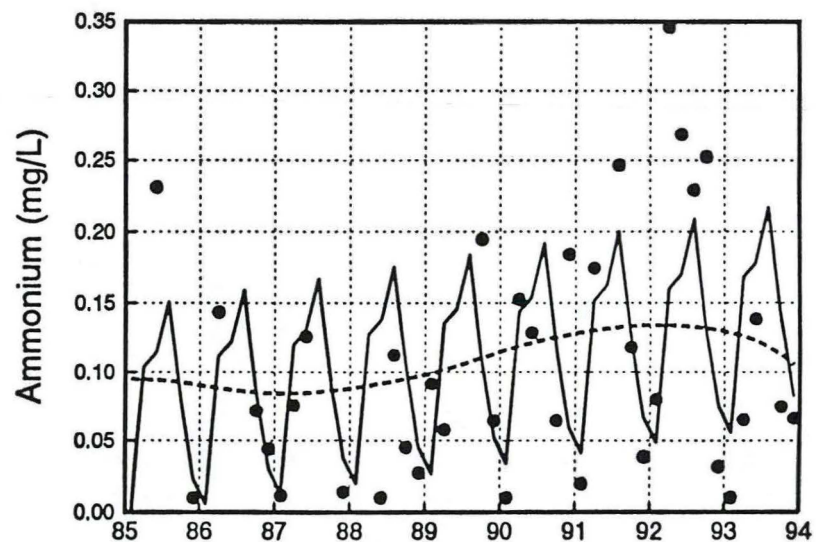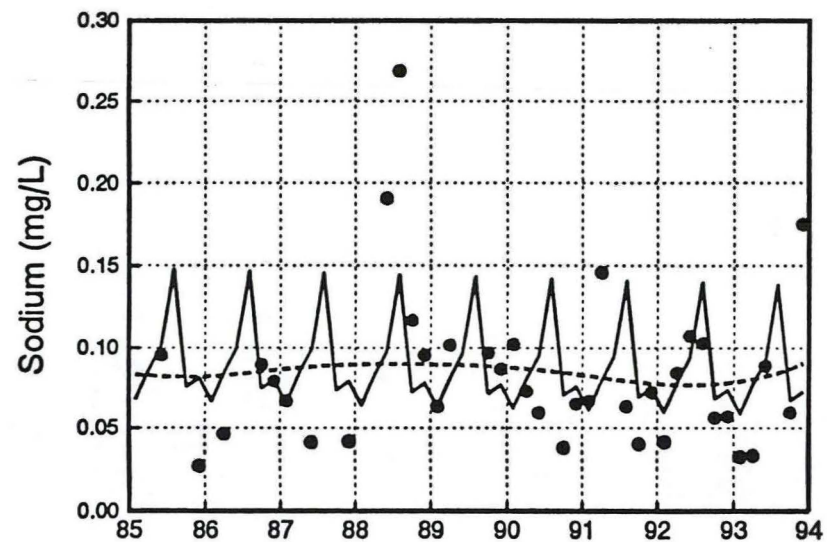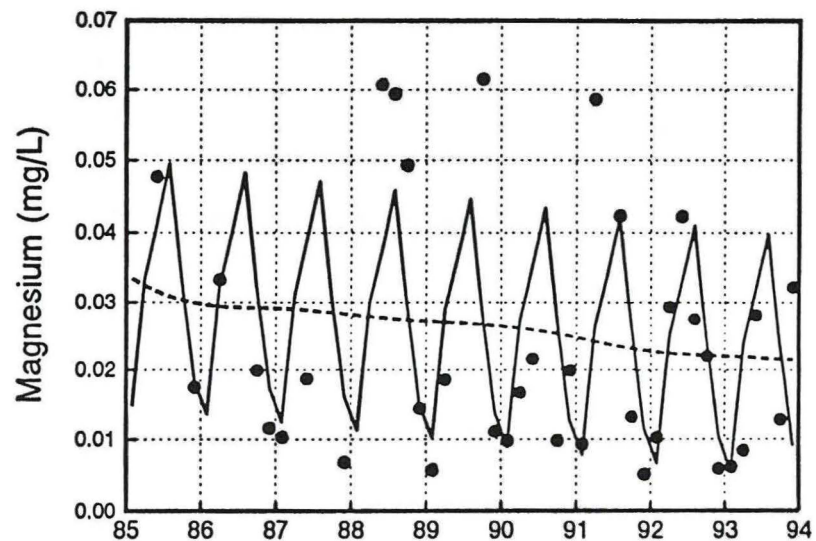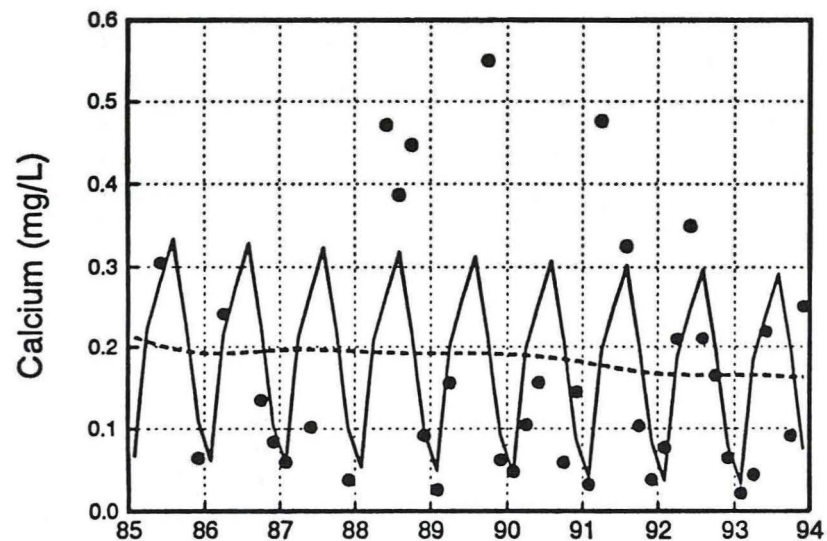
WY98 - Gypsum Creek
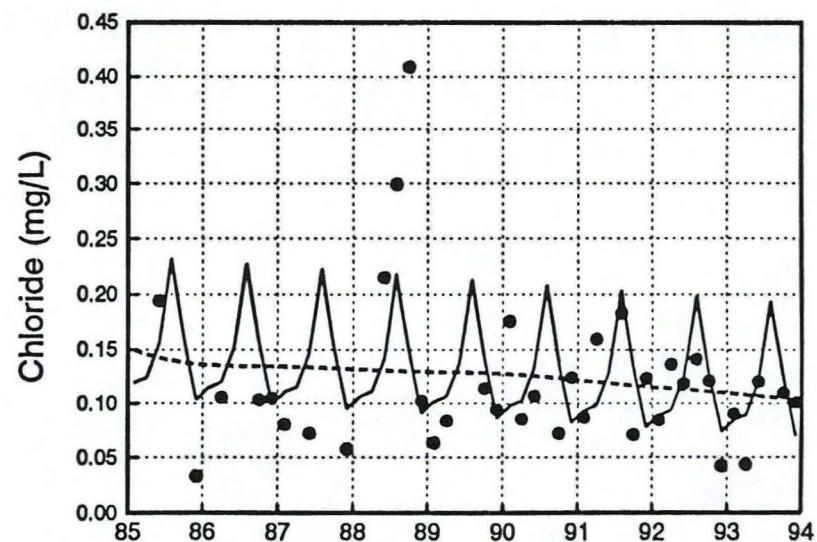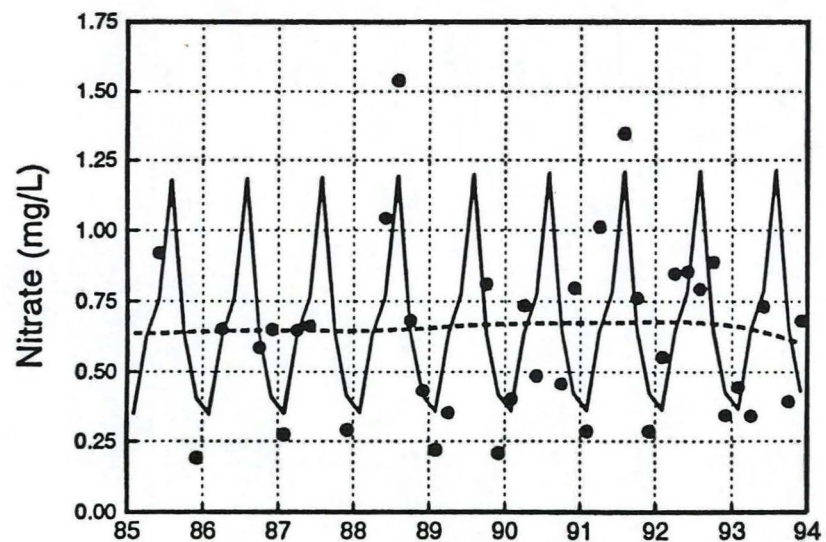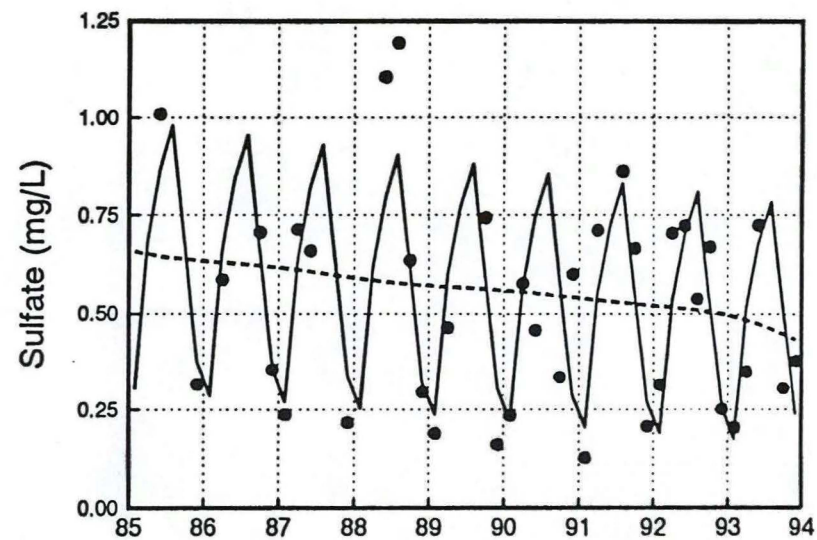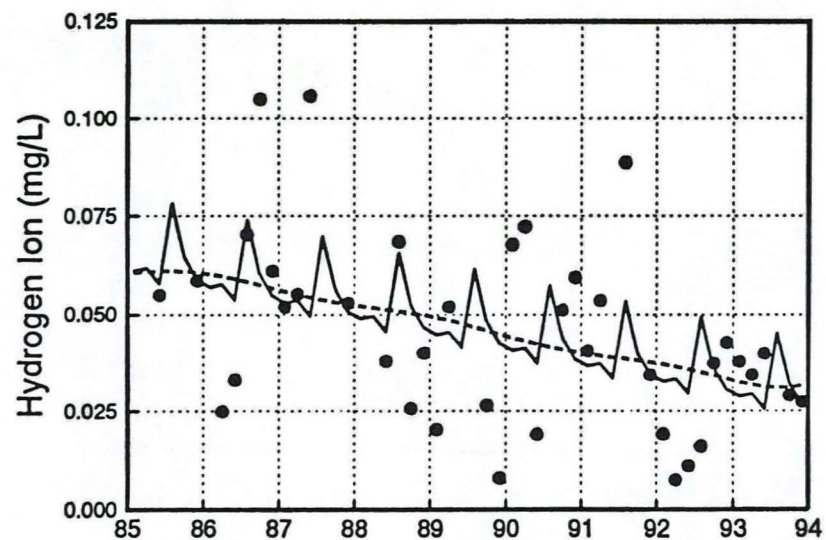
dropped significantly at Sinks Canyon (40%) and at Gypsum Creek (53%), and showed no trend at Pinedale. All three sites showed increases in ammonium concentrations between 1985-1993, of 13%, 76%, and 63%, for Sinks Canyon, Gypsum Creek, and Pinedale, respectively, but none of these increases was significant. Decreases in calcium, magnesium, potassium, and chloride were significant for Sinks Canyon, but not for the other two sites.

Time series of sulfate, nitrate, and calcium deposition at the four NADP sites do not reveal visual trends (Figures 3b-d). Deposition tracks precipitation, however (Figure 3a). Regressions of sulfate and nitrate with precipitation suggest between 40-80% of the deposition of these solutes at all sites was explained by precipitation alone (Table 7). The relation of calcium with precipitation was not as strong; only 10-30% of the variance in calcium was explained by deposition.

3.2.b. Estimates of Deposition at Increasing Elevation: NADP/Isopleth Model

Because of orographic increases in precipitation, deposition is greater at higher elevations. A report prepared for a Forest Service workshop to develop guidelines to

Table 7. Results from regressing nitrate, sulfate, and calcium deposition with precipitation for the four Wyoming NADP sites surrounding the Wind River mountains. Values presented are r^2.

SITE	CALCIUM	SULFATE	NITRATE
Pinedale	0.23	0.59	0.54
Gypsum Creek	0.25	0.44	0.66
Sinks Canyon	0.29	0.61	0.78
South Pass City	0.1	0.67	0.56

evaluating pollution impacts to wilderness areas described an extrapolation technique

to estimate deposition to high elevations (Gibson 1990). NADP precipitation

concentration data were averaged for the four sites surrounding the Wind Rivers for

the years 1987-1989. These were multiplied by 30 year precipitation estimates from

elevational isopleths used by the Soil Conservation Service (now Natural Resources

Conservation Service) to derive deposition at high elevations (Figure 5). The results

show much greater deposition of all solutes at higher elevations due to orographic

increases in precipitation (Table 8).

We applied the NADP/isopleth approach to deposition for calendar years 1992-

1994 (Table 8). The 1987, 1988, and 1989 years were wet, dry, and moderate

precipitation years, respectively. The years 1992 and 1994 were dry, while 1993 was

a wet year (Figure 3a). Interestingly, there was lower deposition during 1993 than the

two dry years 1992 and 1994 due to the lower concentrations in 1993. In 1994

calcium, ammonium, and sulfate deposition were similar to deposition of these solutes

in other years, but nitrate deposition was greater, by at least 2 kg/ha, than any other

year.

3.2.c. Bulk Deposition from Black Joe and Hobbs Lakes

Measured precipitation was generally lower at Black Joe Lake than at Hobbs

Lake for the years 1992 through 1994 (Table 9). About twice as much precipitation

fell at these mountain sites compared with the lower elevation NADP sites. In spite of

the uncertainty associated with mountain precipitation collectors, both sites reported

Figure 5. Precipitation isopleths, in inches, based on elevation (from Gibson 1990).

Precipitation - inches

20-30   30-40   40-50   50-60   60-70

JACKSON

DUBOIS

GROS VENTRE

FITZPATRICK

BRIDGER

PINEDALE

LANDER

POPO AGIE
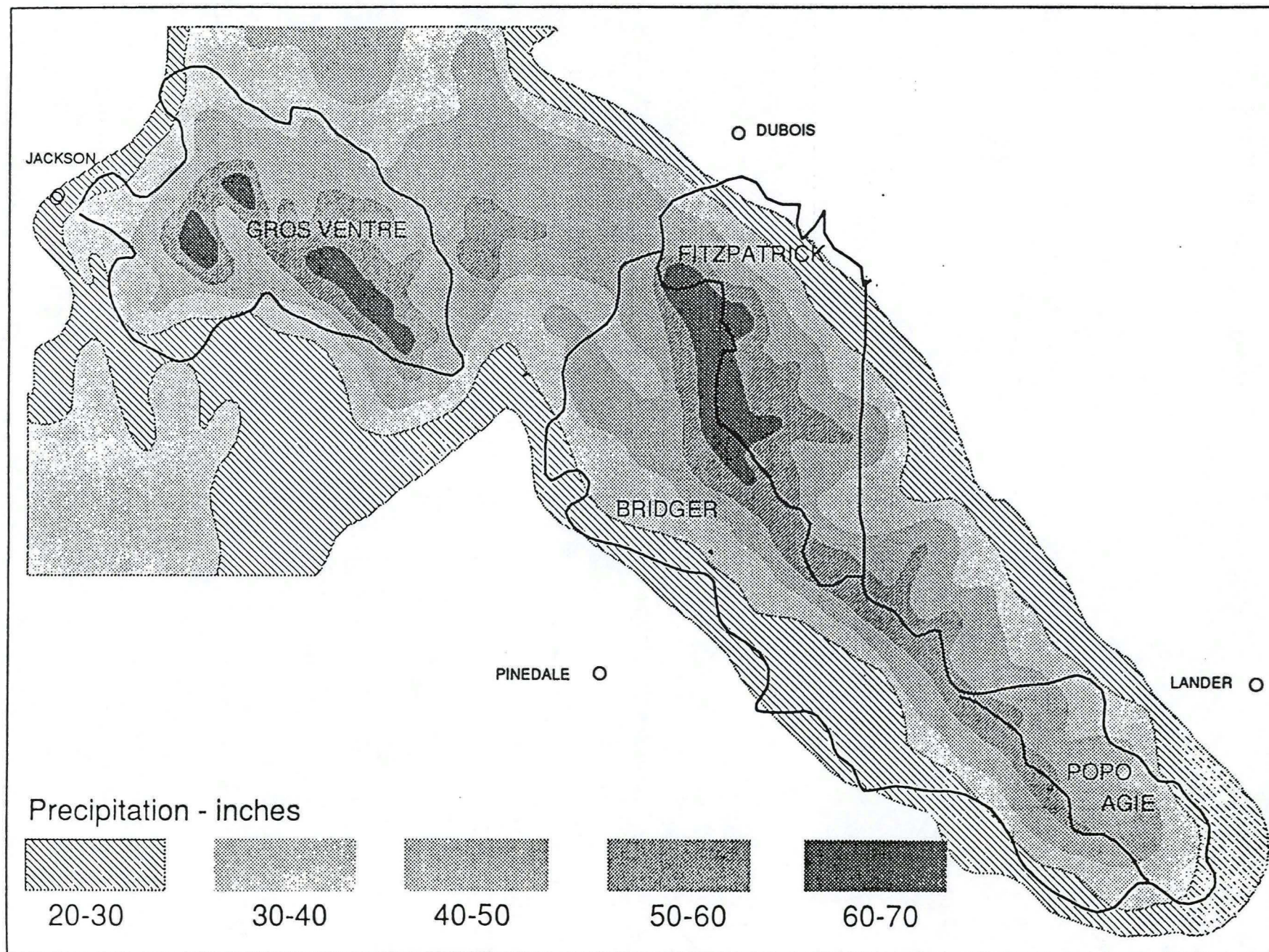
Table 8. Average annual wet deposition with elevation in the Wind River Mountains using 30 year average annual precipitation isopleths and NADP precipitation chemistry. Composite years 1987-1989 are from Gibson (1990). Precipitation is in cm, deposition is kg/ha.

Precipitation	CALCIUM	AMMONIUM	NITRATE	SULFATE
1987-1989 75-100	1.88-2.50	0.75-1.01	4.52-6.02	4.86-6.48
100-125	2.50-3.13	1.01-1.25	6.02-7.53	6.48-8.13
125-150	3.13-3.75	1.25-1.51	7.53-8.99	8.13-9.75
150-175	3.75-4.38	1.51-1.75	8.99-10.50	9.75-11.37
1992 75-100	1.65-2.20	1.35-1.80	5.70-7.60	4.50-6.00
100-125	2.20-2.75	1.80-2.25	7.60-9.50	6.00-7.50
125-150	2.75-3.30	2.25-2.70	9.50-11.40	7.50-9.00
150-175	3.30-3.85	2.70-3.15	11.40-13.30	9.00-10.50
1993 75-100	1.05-1.40	0.90-1.20	4.73-6.30	4.20-5.60
100-125	1.40-1.75	1.20-1.50	6.30-7.88	5.60-7.00
125-150	1.75-1.20	1.50-1.80	7.88-9.45	7.00-8.40
150-175	2.10-2.45	1.80-2.10	9.45-11.00	8.40-9.80
1994 75-100	1.90-2.50	1.28-1.70	6.90-9.20	4.88-6.50
100-125	2.50-3.10	1.70-2.13	9.20-11.50	6.50-8.13
125-150	3.10-3.75	2.13-2.55	11.50-13.80	8.13-9.75
150-175	3.75-4.38	2.55-2.98	13.80-16.10	9.75-11.38

Table 9. Concentrations of solutes in precipitation from bulk collectors located at **Black Joe and Hobbs Lakes, for the years 1992-1994. Concentrations are in µeq/L; measured** precipitation, including rain and snow, is in cm. Average values are arithmetic.

SITE AND YEAR	H	Ca	Mg	K	Na	NH₄	NO₃	Cl	SO₄	Rain	Snow	Ppt'n
BLACK JOE 1992	10.8	16.6	3.0	0.9	4.1	9.8	15.0	3.9	15.0	25.0	57.3	82.3
1993	10.0	22.3	4.4	1.8	8.9	10.5	22.4	5.3	21.8	11.5	78.6	90.1
1994	7.9	19.6	3.7	1.1	4.4	12.2	18.9	3.6	17.8	15.9	34.1	50.0
BLACK JOE AVERAGE	9.6	19.6	3.7	1.3	5.8	10.9	18.8	4.2	18.3	17.5	56.7	74.1
HOBBS 1992	8.4	19.7	4.8	2.3	5.1	4.8	11.2	5.4	13.8	22.2	59.6	81.8
1993	15.8	12.0	2.5	1.0	3.9	5.8	11.5	3.0	11.4	21.4	86.5	107.9
1994	10.6	20.1	3.8	1.0	4.6	8.0	14.3	3.6	14.3	19.2	54.2	73.4
HOBBS AVERAGE	11.8	17.4	3.6	1.4	4.5	6.3	12.4	3.9	13.1	20.9	66.8	87.7

higher precipitation in 1993 than in the other two years, reflecting the same regional precipitation pattern as the lower elevation NADP precipitation sites. Sixty-eight to eighty-seven percent of annual precipitation fell during the non-winter months of June-September. This distribution is similar to the distribution across seasons for the lower elevation NADP sites, but whereas precipitation in winter months at high elevations fell as snow, a greater proportion of precipitation between October and May would fall as rain at the lower elevation sites.

Precipitation was more concentrated at Black Joe Lake by an average of 18 μeq/L, although there was less acidity in the Black Joe bulk collectors (Table 9). Not all solutes were more concentrated in Black Joe precipitation than Hobbs precipitation. The basic cations calcium, magnesium, sodium, and potassium, were of similar concentrations at both sites. Ammonium was nearly twice as high at Black Joe, and nitrate, sulfate and chloride were elevated at Black Joe over Hobbs.

Deposition of calcium, calculated with measured precipitation amounts, ranged 1.85-2.65 kg/ha and 2.09-3.28 kg/ha for Black Joe and Hobbs Lakes, respectively (Table 10). Ammonium ranged from 1.02--1.86 kg/ha, and 0.90-1.65 kg/ha for Black Joe and Hobbs Lakes. Nitrate ranged 5.70-8.48 kg/ha, and 5.33-8.92 kg/ha for the two lakes, and sulfate ranged 3.92-8.14 kg/ha, and 4.36-7.25 kg/ha, respectively. There was no consistency in deposition compared with that expected from NADP site data and precipitation isopleths (Table 8). Except for the high moisture year of 1993, deposition of calcium, ammonium, nitrate and sulfate was lower than the

Table 10. Bulk deposition estimates (kg/ha) from collectors at Black Joe Lake and Hobbs Lake, for the years 1992-1994. Values are derived from measured concentrations and measured volumes in the summer funnel collectors (rain), and the winter cylinder collectors (snow).

SITE AND YEAR	H	Ca	Mg	Na	K	NH_4	Cl	NO_3	SO_4	Total ppt, cm
BLACK JOE 1992	0.09	2.54	0.30	0.78	0.25	1.82	1.00	7.36	6.26	82.3
1993	0.09	2.65	0.34	1.41	0.25	1.86	1.10	8.48	8.14	90.1
1994	0.04	1.85	0.21	0.48	0.22	1.02	0.62	5.70	3.92	50.0
HOBBS 1992	0.07	2.09	0.27	0.74	0.39	0.95	1.38	5.33	4.36	81.8
1993	0.17	3.28	0.27	1.24	0.33	1.65	1.21	8.92	7.25	107.9
1994	0.08	2.41	0.27	0.72	0.21	0.9	0.74	6.08	4.37	73.4

NADP/isopleth model predictions, based on an expected precipitation range of 125-150 cm/y at the bulk collection sites.

3.2.d. Bulk Concentrations Paired with Precipitation Isopleths

Measured concentrations from the Black Joe Lake bulk collector were paired with precipitation isopleths to give another estimate of deposition corresponding to different elevations (Table 11). At 3122 m, precipitation at Black Joe Lake was estimated at between 125 and 150 cm/y. At this precipitation amount calcium deposition ranged between 4.12 and 6.75 for 1992-1994. This range was much greater than deposition calculated with measured precipitation and solute concentrations (Table 10), and also greater than that predicted using the NADP/isopleth calculations. Similarly, ammonium deposition ranged 2.25-3.30, nitrate deposition ranged 11.63-21.00, and sulfate deposition ranged 9.00-15.75 using measured concentrations and the 125-150 cm precipitation isopleth. Predicted deposition using the isopleths was up to twice that with measured precipitation for ammonium, and twice to three times greater for nitrate and sulfate.

4.0 DISCUSSION

4.1. Water Quality

The lake chemistry shown in Table 3 indicates the five Wind River study lakes are low ionic strength, and are vulnerable to deposition of strong acid anions. Acid neutralizing capacity was slightly greater in Black Joe, Deep, and Hobbs Lakes than in Ross Lake to the north and Saddlebag to the south, but all five lakes had ANC values

Table 11. Average annual wet deposition (kg/ha) in the Wind River Mountains using solute concentrations from bulk collectors located at Black Joe Lake and precipitation isopleths from the Soil Conservation Service (after Gibson et al. 1990).

Precipitation	CALCIUM	AMMONIUM	NITRATE	SULFATE
1992 75-100	2.50-3.30	1.32-1.80	6.95-9.30	5.42-7.20
100-125	3.30-4.12	1.80-2.25	9.30-11.63	7.20-9.00
125-150	4.12-4.95	2.25-2.70	11.63-13.95	9.00-10.80
150-175	4.95-5.80	2.70-3.15	13.95-16.28	10.80-12.60
1993 75-100	3.38-4.50	1.43-1.90	10.48-14.00	7.86-10.50
100-125	4.50-5.62	1.90-2.38	14.00-17.50	10.50-13.13
125-150	5.62-6.75	2.38-2.85	17.50-21.00	13.13-15.75
150-175	6.75-7.88	2.85-3.33	21.00-24.50	15.75-18.38
1994 75-100	2.92-3.90	1.65-2.20	8.83-11.80	6.40-8.50
100-125	3.90-4.88	2.20-2.75	11.80-14.75	8.50-10.63
125-150	4.88-5.85	2.75-3.30	14.75-17.70	10.63-12.75
150-175	5.85-6.83	3.30-3.85	17.70-20.65	12.75-14.88

well below the 200 µeq/L threshold value for sensitivity to acidic deposition identified by the EPA (Landers et al. 1986). Wright (1983), and Turk and Spahr (1990) estimate the decrease in ANC for Wind River lakes due to atmospheric deposition of strong acid anions to be no greater than 6-12 µeq/L , a loss similar to that estimated for lakes of the Colorado Front Range. Specific conductance, pH, calcium, magnesium, sodium, ammonium, chloride, sulfate, and ANC were similar in values to lakes of the Colorado Front Range, another cluster of highly sensitive lakes in the Rocky Mountains (Baron 1992, Turk and Spahr 1990).

Three of the five Wind River lakes were included as special interest lakes in the EPA Western Lake Survey (WLS) of 1985, and results of the survey are compared with September and October Forest Service collected samples from 1991-1993 in Table 12 (Eilers et al. 1987). WLS samples had slightly higher pH and conductivity. Base cations were similar between WLS and Forest Service samples. Ammonium was higher in all Forest Service samples, and nitrate was higher in Hobbs and Ross Lakes, but not Deep Lake, where it was below detection limits. Sulfate was similar in Ross and Hobbs Lakes, but higher in the later samples collected from Deep Lake. ANC was somewhat higher in the more recent Forest Service samples. Overall the comparison suggests little, if any, change in water quality.

Most chloride in surface waters has an atmospheric source, and where wet deposition is the major source of atmospheric inputs, lake chloride concentrations should equal or be slightly higher than precipitation concentrations (Turk and Spahr 1989, 1990). Turk and Spahr found lake chloride concentrations of the Wind River

Table 12. Western Lake Survey Data from Deep (ID:4D1-069), Hobbs (ID: 4D1-066), and Ross (ID: 4D1-067) Lakes in the Wind River Mountains of Wyoming (top value in each box) and September and October values from Forest Service collected samples 1991-1993 (bottom value in each box). WLS samples were collected in September and October 1985 (Eilers et al. 1987). WLS equilibrium pH and measured conductivity, and Forest Service field pH and conductivity are presented in this table. There were four Forest Service samples each from Deep and Hobbs Lakes, and five from Ross.

Lake	pH	Cond.	Ca	Mg	Na	K	NH$_4$	Cl	NO$_3$	SO$_4$	ANC
Deep:WLS	7.02	11.8	79.6	13.6	13.5	5.4	0.0	3.7	0.0	27.4	71.4
:91-92	6.80	11.4	83.9	14.0	16.8	5.8	0.4	5.3	0.0	31.85	81.15
Hobbs:WLS	7.14	13.3	86.0	20.2	19.4	6.3	0.0	5.4	0.4	17.5	93.6
:91-92	6.85	11.7	85.3	21.9	22.2	5.7	1.3	5.4	1.4	16.9	102.8
Ross: WLS	7.10	9.9	54.9	15.5	14.4	6.0	0.0	8.0	0.7	21.5	62.4
:91-93	6.70	9.1	59.3	18.2	16.7	6.9	0.4	6.4	1.2	20.0	64.1

mountain lakes to be widely distributed around the mean precipitation concentration of 4-5 µeq/L, suggesting additional sources of chloride to lake basins. Mean chloride (USFS Laboratory values) in Black Joe, Deep, and Hobbs Lakes was only slightly greater (0.5-1.0 µeq/L) than precipitation concentrations. Ross and Saddlebag Lakes had values elevated 2-3 µeq/L over precipitation. These lakes could have trace chloride-bearing minerals in their watersheds, or could receive eolian inputs. Turk and Spahr suggest upwind sources of salts, including the Great Salt Lake and regional salty soils, could contribute chloride to the Wind River mountains, and the contribution could be unevenly distributed (Turk and Spahr 1990).

Mean sulfate concentrations for Hobbs, Ross, and Saddlebag Lakes were similar to the median value of 22 µeq/L for the 53 Wind River lakes sampled as part of the Western Lake Survey (Eilers et al. 1986). The sulfate concentrations for Deep and Black Joe of greater than 30 µeq/L were notably higher than both the median lake

concentration and the median precipitation sulfate concentration. Because the higher concentrations are found in some, but not all, of the west-side lakes, it is likely there are trace sulfur-bearing minerals in the watersheds of these lakes that contribute to the lake sulfur content (Turk and Spahr 1989).

Nitrate concentrations in Wind River lakes were lower than those of some Colorado lakes with mean concentrations of 10-20 µeq/L (Baron 1992, Williams et al. in press). Nitrate values were, however, higher than expected for Black Joe, Ross, and Saddlebag Lakes, suggesting elevated levels of N deposition have increased nitrate concentrations in the water bodies. Because terrestrial ecosystem productivity is generally limited by insufficient nitrogen availability, little or no inorganic nitrogen should escape terrestrial systems to leak into surface waters (Aber et al. 1989, Stoddard 1994, Hedin et al. 1995). A simulation of tundra ecosystem response to increasing nitrogen availability suggested alpine tundra is so limited in ability to retain atmospheric nitrogen due to temperature and possibly other nutrient constraints that nitrogen saturation could have been reached in the Colorado Front Range at about 6 kg N/ha deposition (Baron et al. 1994). Similar tundra response in the Wind Rivers could help to explain the observed lake nitrate values.

The lack of vegetation at high elevations also increases the potential for atmospheric nitrogen to move through or over bedrock and talus into surface waters (Campbell et al. 1995). Without microbial or plant communities to consume and retain the nitrogen, increased deposition should result in increased surface water concentrations.

4.2. Trend Analysis of Deposition

Nationally, sulfate concentrations in precipitation have decreased, as have concentrations of calcium and magnesium (Lynch et al. 1995b). This has caused a decrease in precipitation acidity at some sites, but at other locations the decrease in sulfate has been offset by increases in nitrate. While nitrate concentrations are decreasing generally throughout the country, there are areas of the West where nitrate concentrations are increasing with time (Lynch et al. 1995b). These national trends are found in the vicinity of the Wind River Mountains, where sulfate and hydrogen concentrations decreased at two of three NADP sites, while base cations and chloride decreased at all of the sites. Some of these trends are significant (Lynch et al 1995a). Slight increases in nitrate concentration were reported with time for all three sites, but none of them were significant.

Only five out of 31 NADP sites in the western states Washington, Oregon, Idaho, Utah, Montana, Wyoming, and Colorado reported decreasing nitrate concentration trends for the period 1985-1993, and of those, only one was significant (Lynch et al. 1995a). Twenty six of the sites showed increasing nitrate concentration trends, ten of which were significant over the period 1985-1993. As mentioned before, the three sites near the Wind Rivers increased but not significantly. Deposition amounts are potentially high enough already to cause elevated nitrate leaching in watersheds, and it is prudent to continue precipitation monitoring into the future.

4.3. Elevational Extrapolation

It is always difficult to estimate the amount of deposition at high elevations because of the difficulties in measuring precipitation in windy mountainous environments. The three techniques used here to estimate deposition, the NADP/isopleth model, measured bulk precipitation, and the bulk concentrations and isopleth model, each gave different deposition quantities. There are drawbacks to all the models. The NADP/isopleth model may be flawed because differences in precipitation due to orographic effects at high elevations versus low elevation precipitation patterns may make extrapolation from low to high elevations erroneous. The measured precipitation values of the second model are almost certainly an underestimate of precipitation at high elevations. The third model is probably the most valid of the three, provided the assumption is sound that bulk precipitation is representative of wet deposition.

Despite the shortcomings of each, there are two similarities in the results from all the models that have important ecological ramifications. First, in none of the models does sulfate deposition exceed 10 kg/ha. Sulfate deposition in the Wind Rivers is similar to sulfate deposition in the Colorado Front Range. While elevated over pre-industrial background levels, sulfate deposition does not appear to be great enough to cause a loss of ANC to the point where lakes and streams acidify (Baker et al. 1990). Further, sulfate deposition has decreased with time through most of the Western United States (Lynch et al. 1995a, 1995b).

Second, nitrate deposition is greater than sulfate deposition, and in contrast to sulfate, is high enough to lead to nitrogen saturation and eventually to lake acidification. The lowest estimates of between 5 and 9 kg/ha, from measured bulk precipitation, are similar to those reported from the Colorado Front Range (Baron 1992, Williams et al. in press). Nitrogen deposition in the Colorado Front Range has already caused elevated stream and lake nitrate concentrations (Baron et al. 1994, Campbell et al. 1995, Williams et al. in press). The highest estimates of 11-21 kg/ha, from bulk concentrations and isopleths, bring deposition into the range of the eastern United States, where nitrogen saturation is a serious environmental problem (Aber et al. 1989, Likens and Bormann 1995).

4.4. Trend Analysis of Lake Chemistry

There are no trends of chemical composition with time in the study lakes, with the possible exception of alkalinity and calcium. Calcium increased in four out of five lakes, and the increase in ANC was only significant in Black Joe Lake. Alkalinity decreased slightly in Saddlebag Lake. One can speculate that the increase in calcium may reflect a slight change in weathering processes in several lake basins. Most ANC in dilute waters is bicarbonate alkalinity, and increases in $CaCO_3$ could occur several ways. Since dissolution of $CaCO_3$, or calcite, is very rapid, wet years could weather more calcite from bedrock minerals (Clow et al., in prep.). Alternatively, an increase in wind-blown material that can accompany dry precipitation years could add eolian dust to watersheds, and lead to elevated calcium and ANC in surface waters (Turk and Spahr 1990, Graustein and Armstrong 1983). Calcite is a common wind-blown

mineral in the western United States. Calcium can increase in surface waters in response to acidic anions stripping cations from soils (Reuss and Johnson 1986, Likens and Bormann 1995). An early watershed response to acidic deposition is observed as an increase in base cations in surface waters, in response to cation stripping off the soil exchange. After base cations and alkalinity are depleted from soils, ANC in surface waters decreases rapidly, leading to acidification. Levels of acidity of 70 mol/ha/y were insufficient to cause cation stripping from soils in Idaho (Clayton 1988). Acid inputs to the Colorado Front Range of 140 mol/ha/y were also insufficient to lead to loss of soil cations (Mast et al. 1990). Acid deposition in the Wind Rivers falls between 60 and 80 mol/ha/y, so this does not seem like a likely reason for elevated calcium and carbonate in surface waters. Finally, it is possible that the perceived trend in calcium and ANC is not a trend at all, and the ten year record is too short to perceive longer-term dynamics. At the Hubbard Brook Experimental Forest in New Hampshire, 18 years of record were required to find a statistically significant linear regression for precipitation acidity (Likens and Bormann 1995). Surface waters are complicated in their response by additional upstream processes that mitigate precipitation inputs.

Sulfate concentrations did not increase or decrease in lake waters from 1984-1994. If lake sulfate was derived entirely from atmospheric deposition, this could be interpreted as reflecting stability in atmospheric sulfate deposition.

4.5. Summary

Interpretation of any water quality trends is confounded by changes in the chemical record caused by changing chemical analytical laboratories. However, there do not appear to be trends in water quality attributable to polluted deposition.

Methods of extrapolating deposition to high elevations from precipitation concentrations at low and high elevation collectors converge on the conclusion that sulfate is not a strong acid anion of concern. Deposition of nitrate, however, must be watched closely over the coming years. Nitrate is currently elevated in both deposition and in several of the lakes. Because nitrate deposition can eventually lead to loss of acid neutralizing capacity in surface waters, I recommend that monitoring of low elevation wet deposition at the NADP/NTN sites, bulk deposition at the Black Joe and Hobbs high elevation sites, and water quality monitoring of all five lakes continue. These data not only should be collected, they should be evaluated yearly and compared with previous years in order to maintain continuity in tracking deposition and effects. Lakes and streams of the Bridger-Fitzpatrick and Popo-Agie Wilderness Areas do not exhibit serious water quality problems, but given their low alkalinity and proximity to sources of nitrogen and sulfur oxides, water quality could change rapidly.

5.0 ACKNOWLEDGEMENTS

6.0 REFERENCES

Aber, J.D., K.J. Nadelhoffer, P. Steudler, and J.M. Melillo. 1989. Nitrogen saturation in northern forest ecosystems. BioScience 39:378-386.

Aubertin, G.M., D.S. Bigelow, and B.A. Malo, (eds.). 1990. Quality Assurance Plan: NADP/NTN Deposition Monitoring. National Atmospheric Deposition Program. Natural Resource Ecology Laboratory. Fort Collins CO.

Baker, L.A., J.M. Eilers, R.B. Cook, P.R. Kaufmann, and A.T. Herlihy. 1990. Interregional comparisons of surface water chemistry and biogeochemical processes. pp. 567-614 in: D.F. Charles, ed. Acidic Deposition and Aquatic Ecosystems: Regional Case Studies. Springer-Verlag, New York.

Baron, J. (ed.). 1992. Biogeochemistry of a Subalpine Ecosystem: Loch Vale Watershed. Springer-Verlag, New York.

Baron, J.S., D.S. Ojima, E.A. Holland, and W.J. Parton. 1994. Analysis of nitrogen saturation potential in Rocky Mountain tundra and forest: implications for aquatic systems. Biogeochemistry 27:61-82.

Bigelow, D.S., and S.R. Dossett. 1988. Instruction manual: NADP/NTN Site Operation. National Atmospheric Deposition Program, Natural Resource Ecology Laboratory, Fort Collins, CO.

Bigelow, D.S., D.L. Sisterson, and L.J. Schroder. 1989. An interpretation of differences between field and laboratory pH values reported by the National Atmospheric Deposition Program/National Trends Network monitoring program. Environ. Sci. and Technol. 23: 881-887.

Campbell, D.H., D.W. Clow, G.P. Ingersoll, M.A. Mast, N.E. Spahr, and J.T. Turk. 1995. Processes controlling the chemistry of two snowmelt-dominated streams in the Rocky Mountains. Water Resourc. Res. 31:2811-2822.

Clayton, J.L. 1988. Some observations of the stoichiometry of feldspar hydroloysis in granitic soils. J. Environ. Qual. 17:153-157.

Eilers, J.M., P. Kanciruk, R.A. McCord, W.S. Overton, L. Hook, D.J. Blick, D.F. Brakke, P. Lerrar, M.E. Silverstein, D.H. Landers. 1986. Characteristics of lakes in the western United States: Vol. II Data compendium for selected physical and chemical variables. EPA-600/3-86/054B. U.S. Environmental Protection Agency, Washington, D.C.

Fishman, M.J. and L.C. Friedman. 1985. Methods for determination of inorganic substances in water and fluvial sediments. In: Techniques of Water Resources Investigations of the U.S. Geological Survey, Book 5, Ch. 6. US Government Printing Office, Washington, D.C.

Galbraith, A.F., C. Harrelson, and C. Rawlins. 1991. Acid deposition in the Wind River Mountains: Air quality related values report #2. Bridger-Teton National Forest, Jackson, WY.

Gibson, J.H. 1990. Colorado-Wyoming Wilderness areas wet chemical deposition estimates. National Atmospheric Deposition Program, Fort Collins, CO. in: A.F. Galbraith (ed.) Workshop proceedings-Air quality and acid deposition potential in the Bridger and Fitzpatrick wildernesses. USDA Forest Service, Region 4, Ogden, UT.

Graustein, W.C. and R.L. Armstrong. 1983. The use of strontium-87/strontium-86 ratios to measure atmospheric transport into forested watershed. Science 219: 289-292.

Hedin, L.O., J.J. Armesto, and A.H. Johnson. 1995. Patterns of nutrient loss from unpolluted, old-growth temperate forests: evaluation of biogeochemical theory. Ecology 76:493-509.

Landers, D.H., J.M. Eilers, D.F. Brakke, W.S. Overton, R.D. Schonbrod, R.T. Crowe, R.A. Linthurst, J.A. Omernik, S.A. Teague, and E.P. Meier. 1986. Characteristics of lakes in the Western United States, Vol. 1: Population Descriptions and Physiochemical Relationships. EPA-600/3-86/054a, U.S. Environmental Protection Agency. Washington D.C.

Likens, G.E. and F.H. Bormann. 1995. Biogeochemistry of a forested ecosystem, 2nd Ed. Springer-Verlag, New York.

Lynch, J.A., V.C. Bowersox, and C. Simmons. 1995a. Precipitation chemistry trends in the United States: 1980-1993. Summary Report. National Atmospheric Deposition Program. Natural Resource Ecology Laboratory, Fort Collins, CO. 103 pp.

Lynch, J.A., J.W. Grimm, and V.C. Bowersox. 1995b. Trends in precipitation chemistry in the United States: a national perspective, 1980-1992. Atmos. Environ. 29:1231-1246.

Mast, M.A., J.I. Drever, and J. Baron. 1990. Chemical weathering in The Loch Vale Watershed, Rocky Mountain National Park, Colorado. Water Resour. Resear. 26:2971-2978.

NADP/NTN Data Base. 1994. National Atmospheric Deposition Program. Tape of Weekly Data. National Atmospheric Deposition Program (IR-7)/National Trends Network. July 1978-January 1995. [Magnetic tape, 9 track, 1600 cpi, ASCII]. NADP/NTN Coordination Office, Natural Resource Ecology Laboratory, Colorado State University, Fort Collins, CO.

O'Deen, L., R. Musselman, C. Regan, and M. Conrad. 1994. Quality Control/Quality Assurance Program at the Glacier Lakes Ecosystem Experiments Site (GLEES) in the Snowy Range of Wyoming. General Technical Report RM-0000, Rocky Mountain Forest and Range Experiment Station, USDA Forest Service. Fort Collins, CO.

Peden, M.E. 1986. Methods for collection and analysis of precipitation. Champaign, Ill. Illinois State Water Survey, Contract Report 381.

Reuss, J.O. and D.W. Johnson. 1986. Acid deposition and the acidification of soils and surface waters. Ecological Studies Series 59. Springer-Verlag, New York.

Stensland, G.J. and V.C. Bowersox. 1984. Quality assurance in acid precipitation monitoring through the use of ion balance calculations. In: T.R. Johnson, and S.J. Penkala (eds.) Quality Assurance of Air Pollution Measurements. Air Pollution Control Association, Pittsburgh, PA.

Stoddard, J.L. 1994. Long-term changes in the watershed retention of nitrogen: its causes and consequences. Pp. 223-284 in: L.A. Baker (ed.) Environmental chemistry of lakes and reservoirs. Advances in Chemistry Series 237. American Chemical Society, Washington, D.C.

Turk, J.T. and N.E. Spahr. 1989. Chemistry of Rocky Mountain Lakes. pp. 181-208 in: D.C. Adriano and M. Havas, eds.Acidic Precipitation: Volume 1: Case Studies. Springer-Verlag, New York.

Turk, J.T. and N.E. Spahr 1990. Rocky Mountains. pp. 471-502 in: D.F. Charles, ed. Acidic Deposition and Aquatic Ecosystems: Regional Case Studies. Springer-Verlag, New York.

Welker, M. 1994. Temporal patterns in the chemistry of Wind River Lakes and Four NADP/NTN Sites in Wyoming. Report to the USDA Forest Service. 22 pp.

Williams, M.W., J.S. Baron, N. Caine, R. Sommerfeld, and R. Sanford, Jr. Nitrogen saturation in the Rocky Mountains. Environ. Sci. & Technol. in press.

Wright, R.F. and M. Johannessen. 1983. Predicting acidification of North American lakes, Acid Rain Research Report 4/1983. Report No. 0-81036. Norwegian Institute for Water Research, Oslo, Norway.